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(54) Title: PROCESS FOR REMOVAL OF ORGANIC POLLUTANTS FROM WASTE WATER

(57) Abstract

A porous biomass support system in a bioreactor affords biodegradation of phenolic materials to a level under 20 parts per billion at a hydraulic residence time of about 15 hours with significantly less sludge formation currently possible by available methods. The porous biomass support system comprises a hydrophilic polymer, preferably polyurethane foam, small particles of activated carbon and suitable microorganisms, which are entrapped with the polymer material. The carbon is self-regenerative and does not have to be periodically replaced or replenished. The entire porous biomass support system can operate for extended periods of time without replacement.

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PROCESS FOR REMOVAL OF
ORGANIC POLLUTANTS FROM WASTE WATER

5   RELATED APPLICATIONS

This application is a continuation-in-part
application of United States Patent Application Serial
No. 335,610, filed April 10, 1989.

10
BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to a process for the
15 removal of organic pollutants from waste water. More
particularly, this invention relates to a process for
removal of such pollutants especially substituted and
unsubstituted phenols by aerobic biodegration using a
porous biomass support system in a bioreactor,
20 specifically a fixed bed bioreactor

2. Prior Art
One of the hallmarks of contemporary civilization
25 is that each increment of technological progress
almost invariably is accompanied by a similar
increment of environmental regress. As the pace of
technological advances quickens, so does the march of
environmental deterioration. The realization of
30 environmental damage has occurred only relatively
recently, so that present society sometimes finds
itself burdened with the accumulated sins of the
not-too-distant past. But another hallmark of current
society is its acceptance of the undesirability of
35 environmental degradation coupled with a determination
to minimize and even reverse it wherever possible.
Although the return of ground waters to their pristine
condition of an earlier era is not a realistic goal,

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there is a genuine determination to make our waters as
pure as possible. Environmental agencies have set
limits for many common industrial pollutants, and as
methods of pollution reduction have become more
5 successful in reducing or removing pollutants from
waste water, environmental regulations have become
more stringent, resulting in an ever tightening spiral
whose goal is to reduce pollutants in waste water to
that minimum which is technologically feasible.
10   Among the methods employed to reduce or remove
pollutants, bioremediation constitutes an effective
and highly desirable approach. Quite broadly in
bioremediation pollutants serve as a good source,
generally as a source of carbon and/or nitrogen, for
15 microorganisms. Bacterial metabolism converts the
pollutants to metabolites generally with a simple
chemical structure, sometimes degrading the pollutants
completely to carbon dioxide and water in an aerobic
process, or to methane in an anaerobic process. But
20 in any event, the metabolites usually have no adverse
environmental effects.
      Various bioremediation processes are known. For
example, U.S. Patent No. 4,634,672 describes
biologically active compositions for purifying waste
25 water and air which comprises a polyurethane hydrogel
containing (i) surface active coal having a specific
surface according to BET of above 50 m^2/g, a polymer
having cationic groups and cells having enzymatic
activity and being capable of growth. U.S. Patent No.
30 4,681,852 describes a process for biological
purification of waste water and/or air by contacting
the water or air with the biologically active
composition of U.S. Patent No. 4,634,672. The
experimental examples of these patents indicate that
35 the process is not effective for reducing contaminant
concentrations in the effluent strain to less than 44
parts per million (ppm). This is not acceptable since

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the Environmental Protection Agency (EPA) in some
instances has mandated that concentration for some
contaminants (such as phenol) in the effluent stream
must be as low as 20 parts-per-billion (ppb). (See
5 Environmental Protection Agency 40 CFR Parts 414 and
416. Organic Chemicals and Plastics and Synthetic
Fibers Category Effluent Limitations Guidelines,
Pretreatment Standards, and New Source Performance
Standards. Federal Register, Vol. 52, No. 214,
10 Thursday, Nov. 5, 1989. Rules & Regulations, 42522.
       Both U.S. Patent Nos. 3,904,518 and 4,069,148
describe the addition of activated carbon or Fuller's
earth to a suspension of biologically active solids
(activated sludge) in waste water as an aid in phenol
15 removal. The absorbents presumably act by preventing
pollutants toxic to the bacteria from interfering with
bacterial metabolic activity. The patentees' approach
has matured into the so-called PACT process which has
gained commercial acceptance despite its requisites of
20 a long residence time, compious sludge formation with
attendant sludge disposal problems, and the need to
regenerate and replace spent carbon.
       Rehm and coworkers have further refined the use
of activated carbon in the aerobic oxidation of
25 phenolic materials by using microorganisms immobilized
on granular carbon as a porous biomass support
system. Utilizing the propensity of microorganisms to
grow on and remain attached to a surface, Rehm used a
granular activated carbon support of high surface area
30 (1300 m^2/g) to which cells attached within its
macropores and on its surface, as a porous biomass
support system in a loop reactor for phenol removal.
H.M. Ehrhardt and H.J. Rehm, Appl. Microbiol.
Biotechnol., 21, 32-6 (1985). The resulting
35 "immobilized" cells exhibited phenol tolerance up to a
level in the feed of about 15 g/L, whereas free cells
showed a tolerance not more than 1.5 g/L. It was

postulated that the activiated carbon operated like a "buffer and depot" in protecting the immobilized microorganisms by absorbing toxic phenol concentrations and setting low guantities of the
5 absorbed phenol free for gradual biodegradation. This work was somewhat refined using a mixed culture immobilized on activiated carbon [A. Morsen and H.J. Rehm, Appl. Microbiol. Biotechnol., 26, 283-8 (1987] where the investigators noted that a considerable
10 amount of microorganisms had "grown out" into the aquenous medium, i.e., there was substantial sludge formation in their system.

     Suidan and coworkers have done considerable research on the analogous anaerobic degradation of
15 phenol using a packed bed of micoorganisms attached to granular carbon [Y.T. Wang, M.T. Suidan and B.E. Rittman, Journal Water Pollut. Control Fed., 58 227-33 (1986)]. For example, using granular activated carbon of 16 x 20 mesh as a support medium for microorganisms
20 in an expanded bed configuration, and with feed containing from 358-1432 mg phenol/L, effluent phenol levels of about 0 06 mg/L (60 ppb) were obtained at a hydraulic residence time (HRT) of about 24 hours. Somewhat later, a beri-saddle-packed bed and expanded
25 bed granular activated carbon anaerobic reactor in series were used to show a high conversion of COD to methane, virtually all of which occurred in the expanded bed reactor; P.FOx, M.T. Suidan, and J.T. Pfeffer, ibid., 60, 86-92 (1988. The refractory
30 nature of ortho- and meta-cresols toward degradation also was noted.

     Givens and Sack, 42nd Purdue University Industrial Waste Conference Proceedings, pp. 93-102 (1987), performed an extensive evaluation of a carbon
35 impregnated open-celled polyurethane foam as a microbial support system for the aerobic removal of pollutants, including phenol. Porous polyurethane

foam internally impregnated with activated carbon and
having microorganisms attached externally was used in
an activated sludge reactor, analogous to the Captor
and Linpor processes which differ only in the absence
5   of foam-entrapped carbon. The process was attended by
substantial sludge formation and without any
beneficial effect of carbon.

The Captor process itself utilizes porous
polyurethane foam pads to provide a large external
10 surface for microbial growth in an aeration tank for
biological waste water treatment. The work described
above is the Captor process modified by the presence
of carbon entrapped within the foam. A two-year pilot
plant evaluation of the Captor process itself showed
15 substantial sludge formation with significantly lower
microbial density than had been claimed. J.A.
Heidman, R.C. Brenner and H.J. Shah, J. of
Environmental Engineering, 114, 1077-96 (1988). A
point to be noted, as will be revisited below, is that
20 the Captor process is essentially an aerated sludge
reactor where the pads are retained in an aeration
tank by screens in the effluent line. Excess sludge
needs to be continually removed by removing a portion
of the pads via a conveyor and passing the pads
25 through pressure rollers to squeeze out the solids.

H. Bettmann and H.J. Rehm, Appl. Microbial.
Biotechnol., 22, 389-393 (1985) have employed a
fluidized bed bioreactor for the successful continuous
aerobic degradation of phenol at a hydraulic residence
30 time of about 15 hours using Pseudomonas putida
entrapped in a polyacrylamide-hydrazide gel. The use
of microorganisms entrapped within polyurethane foams
in aerobic oxidation of phenol in shake flasks also
has been reported; A.M. Anselmo et al., Biotechnoology
35 B.L., 7, 889-894 (1985).

Known bioremediation processes suffer from a
number or inherent advantages. For example, a major

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result of increased use of such processes is an ever
increasing quantity of sludge, which presents a
serious disposal problem of increasingly restrictive
policies on dumping or spreading untreated sludge on
5 land and at sea.   G. Michael Alsop and Richard A.
Conroy, "Improved Thermal Sludge Conditioning by
Treatment With Acids and Bases", <u>Journal WPCF</u>, Vol.
54, No. 2 (1982), T. Calcutt and R. Frost, "Sludge
Processing - Chances for Tomorrow", <u>Journal of the</u>
10 <u>Institute of Water Pollution Control</u>, Vol 86, No. 2
(1987) and "The Municipal Waste Landfill Crisis and A
Response of New Technology", Prepared by United States
Building Corporation, P.O. Box 49704, Los Angles, CA
90049 (November 22, 1988).   The cost of sludge
15 disposal today may be several fold greater than the
sum of other operating costs of waste water treatment.
      Use of anaerobic sewage treatment systems has
been offered as a solution to the sludge problem.
William J. Jewwll "Anaerobic Sewage Treatment",
20 <u>Environ. Sci. Technol.</u> Vol 21, No. 1 (1987).   The
largest difference between aerobic and anaerobic
systems is in cellular yield.   More than half of the
substrate removal by aerobic systems can yield new
microbial mass or sludge, the yield under anaerobic
25 conditions is usually less that 15% of the organic
substances removed.   However, anaerobic systems are
limited in the number of substrate that they can
degrade or metabolize such as non-substituted
aromatics (See N.S. Battersby & V. Wilson. "Survey of
30 the anaerobic bidegradation Potential of Organic
Chemicals in Digesting Sludge." <u>Applied &</u>
<u>Environmental Microbiology,</u> 55(2): p. 433-439, Feb.
1989.   This is a significant disadvantage in that most
industrial processes such as coke production and coal
35 tar processing normally produce non-substituted
aromatics as by-products (See J.M. Thomas, M.D. Lee,
M.J. Scott and C.H. Ward, "Microbial Ecology of the

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Subsurface at an Abandoned Creosote Waste Site."
<u>Journal of Industrial Microbiology</u>, Vol. 4, p.
109-120, 1989.

Another disadvantage inherent in some known
5 bioremediation processes is that these processes do
not reduce the levels of organic pollutants to
reasonable levels [preferable less than about 0.1
parts permillion (ppm)] at reasonable residence times
(preferably less than about 24 hours). For example,
10 in the process of U.S. Patent Nos. 5,681,851 and
4,634,672 (See the specific examples), the
concentration of phenol contaminants was not reduced
below about 44 ppm.

An industrially desirable method of removing
15 phenolic materials from waste waters have the
following characteristics. The method would be 1) an
aerobic oxidation achieving 2) effluent phenol levels
less than 0.1 parts per million (ppm) at 3) hydraulic
residence times under 24 hours requiring 4) no
20 activated carbon regeneration or replacement and with
5) substantially less sludge formation than obtained
from currently available technology. None of the
aforementioned art achieved all of the above, nor does
the art give any indication how such a goal can be
25 achieved. We have found that if a specific powdered
activated carbon and phenol-degrading aerobic
microorganisms are employed in a open-celled
hydrophilic polyurethane foam, which is then used as a
porous biomass support system in a fixed bed reactor,
30 each of the foregoing goals are readily attained.
Levels of effluent phenol down to at least 20 parts
per billion can be attained at an HRT of under about
16 hours. Carbon is not physically lost from the
reactor, thus avoiding the need for replacement, and
35 is self-regenerative within the reactor. Sludge
formation is minimal; comparative tests with other
fixed bed reactors show that our immobilized cell

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bioreactor (ICB) produces less than 25 percent the
amount of sludge formed by presently commercially
viable systems. In short, as measured by its
performance characteristics, our invention is a a
5 marked improvement over the prior art; relative to the
prior art, our invention represents a difference in
kind rather than a difference in degree.

Reduced sludge formation attending our process is
neither an incidental nor a minor benefit. A major
10 result of increased wastewater treatment is a never
increasing restrictive policies on dumping or
spreading untreated sludge on land and at sea. The
cost of sludge disposal today may be several fold
greater than the sum of other operating costs of
15 wastewater treatment. Accordingly, the reduction in
sludge levels characteristic of our invention has
immediate, substantial economic benefit and alleviates
the pressures of sludge dumping.

20   THE SUMMARY OF INVENTION
This invention relates to materials for porous
biomass support system (PBSS) and processes for
biological treatment of waste streams, specifically
biodegration of organic and waste streams.

25

DESCRIPTION OF THE DRAWINGS
Figure 1 is an adsoption curve measuring phenol
adsorbed for hydrophilic and hydropholic foams and the
foams impregnated with carbon.
30   Figure 2 is an adsorption curve measuring phenol
adsorbed for a hydrophilic foam and a carbon
impreganted hydrophilic foam.
Figure 3 is an adsorption curve for hydrophobic
foam and carbon impregnated hydrophobic foam.
35   Figure 4a is a 1-pulse C-^{13} (labelled) phenol NMR
1-pulse and cross polarization/magic angle spinning of
carbon impregnated hydrophilic foam after adsorption

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of phenol.

Figure 4b depicts a C-^{13} NMR of carbon impregnated hydrophilic foam after exposure to phenol using cross-polarization of magic angle spinning
5 (CPMAS).

Figure 5a is a CPMAS C-^{13} NMR of a hydrophilic foam.

Figure 5b is a CPMAS C-^{13} NMR if a hydrophobic foam.

10 Figure 6 is a 1-pulse MAS C-^{13} NMR of carbon impreganted hydrophilic foam and carbon impregnated hydrophobic foam after exposure phenol.

Figure 7 is a schematic drawing summarizing the NMR results on phenol adsorption of a carbon
15 impreganted hydrophilic foam.

Figure 8 depicts the response of bioreactors containing polyurethane foam (PUF) supports to schock loads of phenol.

Figure 9 depicts the total phenolic removal by
20 reactors having varied polyurethane foam supports.

Figure 10 depicts the removal of aromatic pollutants by two bioreactors; one having a carbon impreganted hydrophilic foam support and an unimpregnatedd hydrophilic polyurethane support.

25 Figure 11 is a scanning electron micrograph of carbon impregnated foam (Hypol) when activated carbon is introduced during polymerization.

Figure 12 is a scanning electron micrograph of a foam (Hypol) when the carbon is surface impregnated by
30 solvent swelling the foam using ethyl acetate.

DETAILED DESCRIPTION OF THE INVENTION

Much of the work to date in biomediation relates to the use of polyurethane foams in treatment
35 process. This invention focuses on improved biomass support materials, which include polyurethanes, as well as their use as biomass support systems in

bioreactors.

One aspect of this invention relates to discovery that certain polymers can adsorb phenolic pullutants; however, the adsorption of these compounds to polymers can depend greatly upon the composition of the various polymers. In addition, we have discovered that the absorption characteristics of a polymer can be very varied by the presence of absence of activated carbon.

One embodiment of the present invention relates to a biomass support comprising a hydrophilic polymer and activated carbon. In general, these polymers provide a porous biomass support for microorganisms. In preferred embodiments, the polymer is hydrophilic polyurethane foam. Polyurethane foams of the preferred embodiments of this invention can be formed directly from the reaction of di-and/or polyfunctional isocyanate compounds in the polymer along with appropriate catalyst or by a partial reaction of the di-and/or polyfunctional isocyanate compounds with the polyol to form a NCO polyurethane prepolymer. Preferably, the NCO polyurethane prepolymer possesses 3 to 10% of the isocyanate compounds as free NCO groups. Therein, water can be used to catalyze the cross reaction of the remaiming groups to form the urethane foam. The adsorption and/or absorption of organic polutents, e.g. phenol, onto and into the polyurethane foam can be affected by both the type of polyol used as well as the portion of cross-linked isocyanate compounds present in the foam. It is preferred to limit the amount of aromatic groups, specifically aromatic isocyanate compounds, in the hydrophilic polyurethane foam in order to maintain the hydrophilic characteristic of the polymer. Preferably, the hydrophilic polymer contains less than about 30% by weight of aromatic isocyanate. In further preferred embodiments of the invention, the

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hydrophilic polymer has at least 90% by weight of
polyethylene oxide and at least less than about 25% by
weight of aromatic isocyanate. In particular
preferred embodiments, the polyol content of
5 hydrophilic polymer is at least 95% by weight
polyethylene oxide and less than about 20% of aromatic
isocyanate. In the more particularly preferred
embodiments of invention, the polyol content is
greater then about 99% by weight polyethylene oxide
10 and less than about 15% by weight of aromatic
isocyanate. The hydrophilic polymers described above
are combined with activated carbon. The activated
carbon used is generally in powder form. Preferably,
the carbon is added either to the polyol prior to the
15 cross linking reaction with isocyanate or with the NCO
prepolymer prior to reaction with water. The carbon
may also be applied to the foam by mixing carbon in
the foam in the presence of a binder which adheres the
carbon to the foam. Such a binder would be selected
20 so as to not inactivate the carbon once the carbon is
applied.
      The hydrophilic polymer supports for use in the
bioremediation are combined with activated carbon
since the activated carbon can enhance the adsorptive
25 capacity of a polymer, e.g. polyurethane foam, for
organic polutents, which include aromatic pollutants,
such as phenol. Carbon concentrates the pollutants.
Although carbon can be added to hydrophilic polymers
and hydrophilic polymers, only when carbon is combined
30 with the hydrophilic polymers is phenol absorbed and
in a mobile state. Once absorbed in a mobile state,
the phenol is able to interact with carbon. It is
discovered that carbon is not in a "mobile state" when
combined with a hydrophilic polymer, for example
35 polyurethane hydropholic polyurethane foam.
      As shown in Table A, hydrophobic foam and
hydrophilic foam each with 20% powdered activated

carbon have a high adsorption coefficient (i.e. large
capacity to adsorb phenol); however, the Langmuir
adsorption curves and carbon C^{-13} phenol/NMR binding
studies summarized at Table 2 and Figures 1 through 7
5 show that the carbon present in the hydrophilic foam
is able to interact with and in fact absorb and adsorb
phenol while embedded in the foam matrix. On the
contrary, this is not a case with conventional
hydrophobic foams. When carbon is embedded in the
10 hydrophibic foam it has a high capacity to absorb the
phenol without the presence of activated carbon. The
hydrophilic foams, on the other hand, do not have a
high capacity to adsorb phenol without the addition of
an appropriate carbon. The adsorption of C^{-13} phenol
15 to carbon impregnated carbon impregnated hydrophilic
and hydrophobic foams was followed using Magic Angle
Spinning/Cross Polarization NMR Spectroscopy. The
results are shown in Figure 4. Peak A at Fig. 4A
represents the phenol that is absorbed into
20 hydrophilic foam. Phenol shows a "fluid" NMR signal
indicating that it is, in fact, mobile within the
polyurethane, which appears to the phenol molecules as
a viscous liquid. Peak B represents the phenol which
adsorbed to the PAC. This phenol appears as a solid
25 in the NMR and is held tightly by the carbon. Peak C
represents phenol that is adsorbed onto the
hydrophibic phenol. This phenol has a solid signal in
the NMR rather then the liquid signal that was
associated with the phenol in the hydrophilic phenol.
30 There is no phenol signal associated with the
activated carbon that is present in the hydrophobic
foam although the amount of phenol that adsorbs to the
hydrophobic foam is relatively high compared to that
absorbed into the hydrophilic foam. A summary of the
35 results obtained by these studies is depicted at
Figure 7.

        The above results indicate that the hydrophilic

foam behaves as a viscous liquid permitting phenol to diffuse through the foam to the carbon support. It is believed that the "viscous" characteristic is provided by the long chain polymers unit of the hydrophilic

5 foam having limited amounts of rigid aromatic (crystalline) region, but large amounts of sp3 carbon oxygen units due to the polyols. The motions of the long chains (of polyols) are sufficiently rigid to permit the existance of free volume and promote the

10 migration of phenol from one free volume unit to the other (See Figure 4A). Because of the mobile phenol and viscous polyurethane foam, the phenol is adsorbed by the polymer and diffuses to the carbon throughout the foam, wherein the phenol is exposed to

15 microorganisms present throughout the foam.

In order to maximize the benefit of activated carbon in a porous biomass support system, the carbon employed should have an effective affinity for aromatics, specifically phenols. The affinity of the

20 carbon is measured by adsorption of phenol and whether it follows the Langmuir absorption curve. An effective carbon follows the Langmuir adsorption curve. The Langmuir curve describes the adsorption of adsorbents as a monolayer into the absorbent.

25 This can be described mathematically as;

$$Q = \frac{CN}{C + K_d}$$

30

35

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where:

Q   is the amount of phenol per unit of
adsorbent.

5   C   is the phenol concentration in solution at
equilibrium conditions.

N   is the maximum adsorbable amount of phenol
at saturation conditions.

10

K_d is the equilibrium phenol concentration
when Q = N/2.

The values of N and K_d can be determined from a plot
15 of C/Q versus C thus:

$$C/Q = C/N + K_d/N$$

where:

the X intercept + $-K_d$
20   the Y intercept + K_d/N

the K_d value reflects the carbon infinity for phenol.
The carbon selected should exhibit a K_d value of at
least about 0.001 mg/L.   Preferably the K_d value
25 ranges from about .001 to 300 about mg/L.   More
preferably the K_d value ranges from about 10 to about
150 mg/L.   In particularly preferred embodiments, the
K_d ranges from about 10 to about 100 mg/L.   It is
important to optimize the K_d value since the infinity
30 of microorganism phenol, generally indicates as K_s,
will generally be less then about 300 gm/L.
In order to optimize interaction between the
activated carbon and the biodegradative
microorganisms, the K_d of the carbon need to be
35 slightly higher than the K_s of the micro-organism.   If
the K_d of the carbon is well below that of the
micro-organism the carbon will act to tightly bind the

organic substrates from the liquid phase but will not
release them at a concentration at which the bacteria
will have a high substrate utilization rate. If on
the other hand the K_d of the carbon is very large
5 compared to the K_s of the micro-organisms there will
be a poor buffering effect on highshock loads of
phenol and when the phenol concentration is lower and
approaches the K_s of the micro-organisms, the carbon
will have a poor ability to concentrate phenol at its
10 surface and thus stimulate microbial growth. An
effective range of K_s/K_d ratios is between 1:1 and
1:50. The more preferred range is between 1:1 and
1:20. The most preferred range is between 1:1 and
1:10. Ks values and other biomass parameters are
15 discussed in the following publications which are
incorporated herein by references (i) D. Orhon et
al., "The Effect of Reactor Hydranlics and the
Performance of Activated Sludge Systems - I. The
Traditional Modelling Approach" Wat. Res Vol 23, No.
20 12 pp. 1511 and 1512 (1989), (ii) Ren Der Yan et al.,
"Dynamic and Steady State Studies of Phenol
biodegradation in Pure and Mixed Cultures",
Biotechnology and Bioergineering, vol XVII, see pp.
1211-12 (1975) and (iii) Spectra, Jr., "Sensitivity
25 Analysis of Biodegration/Adsorption Models" Journal of
Environmental Engineering, Vol. 116, No. 1 see pp.
32-39 (February 1990).
      In particular preferred embodiments of the
invention, the activated carbon is selected from wood,
30 charcoal and anthracite coal. Wood charcoal is more
preferred since it may have an affinity for phenol
which approaches the affinity of phenol-degrading
microorganisms currently available, allowing
maximization of interaction between the phenol and
35 microorganism.
      The porous biomass support system (PBSS) is at
least about 5% by weight of activated carbon (based on

the total weight of the carbon and polymer support).
Preferably, the PBSS is from about 5 to about 85% by
weight of activated carbon. More preferably, the PBSS
is at least about 10% by of activated carbon. Most
5   preferably, the PBSS is about 20 to about 40% by
weight of activated carbon. In addition to activated
carbin, inert fillers can be employed in the biomass
support; however, our biomass system is operable in
the absence or substantially absence of fillers. When
10 employed, the filler material is added prior to
forming the open-celled foam support.

     The microorganisms which are used in the practice
of this invention are aerobic microorganisms selected
to degrade the pollutants of interest in ways well
15 known to those in the art. Thus, cultures isolated
from the pollutant-containing waste streams themselves
usually are enriched and subsequently incorporated
into the PBSS. Conventional microorganisms used for
degration and methods for their selection are broadly
20 known. The PBSS preferably, is prepared by forming
the foam in the presence of a suspension of powdered
activated carbon and suitable microorganisms. Thus,
for example, a suitable polyurethane foam precursor
can be mixed with an aqueous suspension of powdered
25 activated carbon and aerobic pollutant-degraded
microorganisms, often in the presence of blowing or
foaming agents such as carbon dioxide or surfactants,
generally with vigorous mixing at the beginning of
polymerization followed by quiescence of permit good
30 void formation. The foam as produced is then cut into
an appropriate particle size and loaded into a
bioreactor. The pollutant-containing aqueous feed is
pumped through the reactor, generally in an up flow
configuration. It is important for a reactor to be
35 aerated to provide the necessary oxygen-rich
environment for proper microbial metabolism and
pollutant degradation. Oxygen generally is

incorporated along with the feed at the bottom of the
reactor, when the reactor is run in an up flow
configuration, so as to afford an aqueous stream
saturated, or nearly saturated, in oxygen. A minimum
5 dissolved oxygen level of at least 2 mg/L is
desirable, and an oxygen level of 5 mg/L or higher is
preferably.

The porous biomass supported systems of this
invention can be used in any bioreactor: a continuous
10 stirred-tank bioreactor (CSTBR), fixed-bed or
pinked-bed bioreactor (PBBR) or fluidized-bed reactor
(FBBR).

In a preferred embodiment, the porous biomass
support system (PBSS) is employed in a fixed bed
15 bioreactor. In such a reactor, the PBSS is an
open-celled hydrophilic foam, e.g. polyurethane foam
having entrapped within its pores powdered activated
carbon and aerobic pollutant-degrading
microorganisms. The microorganisms can be added prior
20 to the polymerization or cross-linking of the foam or
thereafter. When added after preparation of the foam,
the PBSS is treated or "loaded" with microorganism.
The PBSS is loaded by adding microorganisms to the
reactors packed with the PBSS, optionally along with
25 organic pollutant, and the reactor contianing
supports, microorganisms and pollutant are incubated
in a batch mode so that a large population of
microorganisms develops within the reactor. A small
proportion of these microorganisms will attach to the
30 surface of the PBSS. Fresh medium containing organic
pollutant then pumped through the reactor. The
majority of the unattached microorganisms are removed
by the flow of medium through the reactor but the
attached microorganisms grow and multiply and in doing
35 so form a firmly attached "bioflim" of microbes and
extracellular polymer which entraps more
microorganisms within the pores and on the surface of

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the PBSS.

The carbon concentrates (as shown by NMR) pollutants on its surface. If the carbon were macroporous with pores of a size to accommodate the
5 microorganisms, and if carbon were of a small particle size with a high surface area, we reasoned that the proximity of microorganisms to the locally high concentration of adsorbed pollutant would result in their faster ad more complete degradation. This would
10 afford lower effluent pollutant levels while "protecting" microorganisms from the toxic effects of pollutants. The "immobilization" of bacteria and carbon within the pores of the foam prevents the physical loss of carbon and tends to minimize sludge
15 formation, that is, growth of the microorganisms into the aqueous feed. The PBSS in a fixed bed reactor then provides the high concentration of biomass permitting a relatively low hydraulic retention time.

Stated somewhat differently, at levels above 1-5
20 pmm microorganisms utilize phenol rapidly because of the high binding constants between the microorganisms and phenol, but at levels under 1 ppm utilization is slow and phenol utilization is a lengthy process. The carbon in our PBSS concentrates phenol in the vicinity
25 of microorganisms; the local concentration of phenol as seen by the microorganisms is very high, leading to higher rates of phenol utilization.

The porous biomass support system of our invention is unique in the way it combines foam,
30 carbon, and microorganisms. The invention as described more fully within combines the aforementioned porous biomass support system in a fixed bed operation to afford low phenol effluent levels at a low hydraulic residence time and with
35 significantly less sludge formation than previously attainable. The invention thus affords advantages of considerable industrial merit not previously

attainable by currently available systems.

The organic pollutants which may be degraded by the use of our invention include phenolic material as a major class. Members of this class include phenol

5 itself, the cresols, resorcinol, catechol, halogenated phenols such as 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2.4-dichlorophenol, pentachlorophenol, nitrophenols as 2-nitrophenol and 4-nitrophenol and 2, 4 dimethylphenol. Another important class or organic

10 pollutants consists of aromatic hydrocarbons, such as benzene, toluene, the xylenes, ethylbenzene, and so forth. Polynuclear aromatic hydrocarbons are an important subclass as represented by naphthalene, anthracene, chrysene, acenaphthylene, acenaphthene,

15 phenanthrene, fluorene, fluoranthene, naphthacene, and pyrene. More generally, the method within can be applied to streams containing organic pollutants without limitations, so long as they are capable of being degraded by aerobic microorganisms.

20 The pollutants which are to be biodegraded in the practice of this invention typically are found in aqueous waste streams at industrial manufacturing facilities. For example, phenol is found in waste streams of phenol manufactures, of phenol users as

25 phenol resin producers, of coal tar processing facilities, of wood pulping plants and other facilities practicing delignification. This is not to say that the process can or must be practiced only on such streams. The process which is the invention

30 herein may be practiced on any aqueous feed containing levels of organic pollutants which are to be reduced and which may be greater than that permitted by the environmental protection agency.

The key to our process is the passage of an

35 aqueous feedstock under oxygen rich conditions through a fixed bed reactor of porous biomass support system. The PBSS which is the core of our invention has three

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elements; an open-celled hydrophilic foam, powdered
activated carbon having an effective affinity for
organics entrapped within the foam, and viable,
aerobic, pollutant-degrading microorganisms also
5 entrapped within the interior of the foam.
Incorporation of powdered activated carbon within the
foam prevents its physical loss in fixed bed reactor
operation, obviating the need for periodic replacement
or replenishment of carbon, and also facilitates its
10 bioregeneration. It is postulated that the entrapment
of microorganisms within the foam, especially in close
proximity to the powdered activated carbon, is
responsible in part for the low sludge formation
accompanying the practice of this invention, and also
15 is responsible in part for the low residual levels of
pollutants in the effluent, reasons for which have
been stated above in the discussion of our working
hypothesis of this invention.

    The foam used in the practice of this invention
20 is a particulate open-celled foam to accommodate feed
flow in the fixed bed configuration. That is, it is
important for the pollutant-containing aqueous feed to
flow through the interior of the foam. For the same
reasons it is desired that the foam has high
25 macroporosity; foam desirably are at least 2
millimeters, and preferably are on the order of 5-6
millimeters in size. The foam also needs to be
resistant to the shear forces and abrasion present in
a fixed bed reactor, and should have good crush
30 strength. The foam is desirably semiflexible, with a
density of under about 2 pounds per cubic foot for
optimum economic feasibility. However, higher density
foams, of 4-5 pounds per cubic foot or even higher,
are usable. It needs to be realized that foam density
35 is related to the economics of the invention and not
to its performance; the invention may be practiced
with a large range of foam density, even if certain

ranges may present distinct economic advantages.

As noted the foam can be prepared in the presence
of a suspension of powdered activated carbon and
aerobic, pollutant-degrading microorganisms so as to
5 entrap both of the latter within the interior of the
foam. When prepared the PBSS contains at least 5
weight percent, and up to about 85 weight percent,
preferably not greater than 50 weight percent, of
activated carbon on a dry basis. When activated
10 carbon is present at a level under about 5% its
effectiveness is reduced to a point where the
resulting PBSS is only marginally advantageous. At
levels above about 50 weight percent incoporation of
activated carbon the foam becomes fragile, losing its
15 structural integrity and becoming easily physically
damaged. Most often the PBSS when prepared contains
at least about 10 weight percent activated carbon, and
usually contains from about 20 up to about 40 weight
percent porous activated carbon.

20   The powdered activated carbon has a surface areas
at least about 500 m^2/g, preferably at least about 700
square meters per gram, and is of a size such that at
least 70% of the carbon particles are smaller than
about 44 microns, that is, a minimum of 70% pass
25 through a 325 mesh sieve. The powdered activated
carbon has as high a pore volume as is practical, at
least 0.5 cc/g, typically at least 0.7 cc/g, with as
great a porosity as possible contributed maximized the
concentration of microorganisms in the immediate
30 proximity of the activated carbon surface. Typical
powdered activated carbons used in the practice of
this invention have a surface area 700-1000 m^2/g, pore
volume 0.7-1o cc/g, with 70-100% of the particles
under 44 microns in size. Although these correspond
35 to characteristics of commercially available material,
our invention per se imposes no such limitations. In
particular, high surface area carbons, even up to

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1500-2000 m^2/g, with as high a pore volume as possible
are quite desirable for us in our process.

The pollutant-containing aqueous feed with
dissolved oxygen then be passed through the fixed bed
5 of the PBSS. An hydraulic residence time of under
about 30 hours, generally less than about 24 hours,
and usually no more than about 15 hours, suffices to
attain an effluent phenol level of under 0.1 parts per
million, usually under 20 parts per billion. The
10 particular hydraulic residence time depends upon the
amount of phenolic materials in the feedstock,
operating temperature, the presence of other materials
in the feedstock, operating temperature, the presence
of other materials in the feedstock, the density of
15 microorganisms in the fixed bed, and so forth. The
low hydraulic residence time is a consequence of both
the particular PBSS used and the fixed bed
configuration. The low level in the effluent is a
consequence of the presence of activated carbon in the
20 particular configuration of the PBSS used. The low
sludge level is a consequence of the particular PBSS
in a fixed bed configuration.

The pH of the pollutant-containing feed may need
to be adjusted for optimum biodegradation. Nutrients,
25 and especially phosphate and ammonium salts, any need
to be provided, but sufficient amounts often are
present in the aqueous feed to satisfy minimum
requirements of the microorganism.

PBSS of our invention can be used over extended
30 periods of time without replacement or maintenance of
any type. It is anticipated that in most cases the
initial charge may be used for at least one year and
up to perhaps five years before replacement becomes
necessary. Throughout this time the reactor should
35 operate with significantly less sludge formation than
that from currently available systems, affording
important advantages in sludge disposal costs. A

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comparison of representative levels of sludge
production in several biological treatment systems is
summarized in the following table, where sludge
production is measured per unit reduction of COD
5 (chemical oxygen demand).

SLUDGE PRODUCTION IN BIOLOGICAL TREATMENT SYSTEMS

System	Sludge Production (kg dry wt sludge/metric ton COD consumed)
Aerobic activated sludge	400 – 600 (a)
Anaerobic digester	20 – 150 (a)
Sybron biotower	200 – 300 (b)
This invention	30 – 100 (b)

(a)   R.E. Speece, "Anaerobic Biotechnology for
      Industrial Wastewater Treatment", Environmental
      Science and Technology, Vol. 17, p416A – 427A,
20   1987

(b)   Experimental results; cf. Example 8

      In practice, the method of our invention can
25 reduce phenol levels to under 0.1 ppm, and generally
    to under 20 ppb, with sludge formation of no more than
    100 kg dry weight sludge, often only 30 kg dry weight
    sludge, per metric ton total chemical oxygen demand
    consumed.
30   The following examples are merely illustrations
    and representative of our invention which is of
    considerably larger scope. These examples should not
    be considered limiting in any way.
      In the examples and Figures generated therefrom,
35 the materials used for the hydropholic foam is a
    polyurethane prepolymer (Hypol) having a polyol
    content greater than 90% (approx. 100%) polyethylene

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oxide and an aromatic iso-cyanate contact of less than
15% by weight.

The hydrophobic polyurethane foam (General Foam)
has a polyol content of less than 80% by weight
5 (polyol is approximately 50% polyethylene oxide/50%
polypropylene oxide and the aromatic isocyanate
(toluene disocyanate) content of approximately 25 to
35% Powdered activated carbon is Calgun PAC type WPX.

Example 1: Effective Impregnation of
10   Polyurethane Foams using
          Powdered Activated Carbon (PAC)

The effectivness of impregnating polyurethane
foams with Powdered activated carbon to enhance the
adsorptive capacity of the foam for phenolic
15 pollutants was determined for a hydrophilic
polyurethane (hypol) with a low degree of TDI
cross-linking, a Polyether diol with ethylene oxide
content of greater than 90% and a TDI content of less
than 15% by weight and a hydrophobic polyurethane
20 (General Foam) with high degree of cross-linking, a
polyether diol with ethylene oxide of less than 80%
and a TDI content of approx. 25% to 35% by weight.

The powdered activated carbon was blended with
the polyol precursor or prepolymer prior to foaming at
25 a concentration of 20%.

The absorption co-efficeint of the polyurethane
itself and the polyurethane impregnated with PAC for
phenol was determined by the addition of foam block of
approx. 3/8 inch cube into a solution of phenol in
30 distilled water. The adsorption co-efficient can then
be calculated thus:

$$\text{adsorption coefficient (A)} = \frac{\text{gm phenol remaining/gm water}}{\text{gm phenol absorbed}}$$
35   gm adsorbent

The adsorption coefficeints of the umimpregnated
and impregnated polyurethanes were determined to be:

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Table A

Foam Type	Á constant
Hydrophilic Foam	9.0
Hydrophilic Foam with 20% PAC	74.5
Hydrophobic Foam	62.6
Hydrophobic Foam with 20% PAC	84.4

It was unexpectedly found that the hydrophobic foam had a high capacity to adsorb phenol even without the impregnation with PAC. Furthermore the PAC impregnation did not lead to a significantly greater adsorptive capacity for phenol over the non impregnated hydrophobic foam. The Langmuir adsorption curves for the umpregnated and impregnated polyurethane foams were determined to by ploting C/Q versus C to determine N and K_d values for the Langmuir adsorption.

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Table B

Hydrophilic		Hydrophilic 20% PAC		Hydrophobic		Hydrophobic 20% PAC	
C	Q	C	Q	C	Q	C	Q
55	0.0006	3	0.0221	62	0.0040	47	0.0050
103	0.0015	16	0.0496	121	0.0080	87	0.0110
288	0.0029	94	0.0885	291	0.0210	200	0.0300
548	0.0058	490	0.1169	615	0.0390	489	0.0510
2192	0.0254	1484	0.1614	1426	0.0570	959	0.1400
3174	0.0411	2526	0.1939	2770	0.1230	1724	0.2280
3884	0.0488	3374	0.2596	3984	0.2020	2967	0.3030

Plots of Q versus C and semi-reciprocal plots of C/Q versus C indicate that only the PAC impregnated hydrophilic polyurethane follows the Langmuir adsorption curve. A number of different carbons were evaluated for Langmuir adsorption of phenol. The following results were obtained:

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Table C

Carbon Type	N (gm phenol / gm carbon)	K_d (mg / L)
Germantown Lampblack	weak, non-Langmuir adsorption	-
Bone Char	Weak, non-Langmuir	-
Wood Charcoal	0.2281	90
Anthracite Coal	0.3305	120

Of the four carbons tested only the wood charcoal and the anthracite coal PACs showed Langmuir type adsorption curves for phenol. The adsorption parameters of the hydrophilic polyurethane impregnated with these carbons were determined to be:

Table D

Foam/PAC	N (gm phenol / gm foam/PAC)	K_d (mg / L)
Hydrophilic Foam + 20% Wood Charcoal PAC	0.0266	52
Hydrophilic Foam + 20% Anthracite Coal PAC	0.0383	107

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Example: 4 Response of Bioreactors
Containing Polyurethane
Foam Supports to Shock Loads of Phenol

The following example shows the unexpected
5 superior performance of hydrophilic polyurethane foam
impregnated with activated carbon over conventional
hydrophobic polyurethane foam and same foam
impregnated with activated carbon with regards to
shock loading of bioreactors with phenol. The
10 comparison of the foams is shown in the following
Table E

Time (days)	Phenol Concentration (ppm)			
	Inlet Wastewater	Hydrophobic PUF	Hydrophobic PUF + PAC	Hydrophilic PUF + PAC
1	105	0.005	0.003	0.013
4	130	0.003	0.002	0.004
5	1100	228	278	113
6	1330	4	18	0.021
7	1210	0.009	0.008	0.005
8	1300	0.008	0.008	0.005
14	1160	0.121	19	0.189

The supports were evaluated in glass columns of
dimensions 64 cm height x 3.4 cm diameter. The
columns were packed with foam blocks of approximately
1 cm^3 in size. Phenol containing water was pumped
5 into the bottom of the column and exited from the
top. Air was sparged from the bottom of the column
using a ceramic sparging stone and exited the reactor
from the top also. The flow rate of water through the
reactors was such that the hydraulic residence time
10 was 12 hours. Phenol levvels in the effluent from the
reactors was determined by colorimetric assay.

The results from this study (Fig. 8) showed that
the carbon impregnated hydrophilic foam supports
enabled the bioreactor to produce an effluent of
15 significantly lower phenol concentration when compared
to the bioreactors employing hydrophobic foam or
hydrophobic foam impregnated with activated carbon.
There was in fact little difference between the
reactor with hydrophobic foam only and the reactor
20 containing carbon-impregnated foam.

Example 5: Total Phenolics Removal from
Coal Tar ProcessingWastewater using bioreactors
with Polyurethane Foam Supports

25   The following example unexpectedly shows the
superior performance of carbon impregnated hydrophilic
foam used as a support in bioreactors for the removal
of total phenolics foam without carbon. Twenty gallon
glass tanks were used as bioreactors. The tanks were
30 filled with foam blocks of approximately 1 cubic inch
in size. The packed bed reactor was sparged with air
by means of perforated tubing that ran across the
bottom of the tanks. Wastewater from a coal tar
processing plant, containing a multitude of phenolic
35 and other aromatic pollutants, was fed to the
bioreactor as such a rate that the hydraulic residence
time was approximately 24 hours. The following
results were obtained:

- 30 -

TABLE F

Time (days)	Total Phenolics Concentration (ppm)		
	Inlet Wastewater	Hydrophilic PUF	Hydrophilic PUF + PAC
1	750	4.8	1.5
4	600	25.0	5.0
11	700	6.0	2.4
22	475	5.0	1.2
27	550	6.0	1.6

The results (Fig. 9) show that the bioreactor
that employed the carbon impregnated hydrophilic
polyurethane supports produced an effluent with a
significantly lower level of total phenolics compared
to the bioreactor that used hydrophilic foam that was
not impregnated with carbon.

The removal of specific aromatic pollutants by
the bioreactors was determined using solid phase
extraction and GC/MS. The following results were
obtained:

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TABLE G

Time (days)	Concentration (ppb)					
	Hydrophilic PUF			Hydrophilic PUF + PAC		
	Phenol	2,4-Dimethyl Phenol	Naphthalene	Phenol	2,4-Dimethyl Phenol	Naphthalene
1	14	171	59	20	18	13
4	7,711	590	660	19	98	12
11	43	257	438	13	32	64
22	12	140	81	47	3	2
27	32	165	134	20	3	4

The results (Fig. 10) show that the bioreactor that employs the hydrophilic polyurethane foam impregnated with carbon produces an effluent that is lower in substituted phenol and napthalene as well as phenol compared to the foam without carbon addition.

EXAMPLE 6
Preparation of the Porous Biomass Support System.

A. Preparation of bacterial cluture. To prepare bacterial inoculum adapted to the waste stream that is to be treated, enrichment cultures were set up by adding to samples of the waste stream 100 mg/L ammonium sulfate and 25 mg/L of sodium phosphate

followed by adjustment of pH to 7.0. One hundred mL
portions of the foregoing sample were dispensed into
250 mL flasks and inoculated with soil or sludge, then
incubated at 25°C on a rotary shaker (250 rpm) for 7

5 days. At this time 1 mL subcultures were dispensed
into new wastewater samples and incubated for another
7 days. Cultures were then maintained under these
conditions prior to foam manufacutre.

   B. <u>Foam Preparation</u>. The polyurethane used to
10 manufacture the biofoam was a toluene diisocyanate
polyether prepolymer supplied by W.R. Grace under the
trade name Hypol. Foaming occurs upon reaction with
water, and the pore structure of foam can be altered
by the addition of surfactants as well as auxiliary

15 blowing agents such as chlorofluorocarbons or
exogenuous carbon dioxide to afford interconnected
pores of at least 2 millimeter size. The following
procedure is typical.

   Five gallons (50 lbs) of polyurethane prepolymer
20 (HYPOL 2000) was added to a mixing vessel of
approximately 100 gallons capacity. Twenty-five
pounds of activated carbon (Calgon PAC type WPX), 2 mL
of tween 80 surfactant, and 20 grams of sodium
bicarbonate were mixed with the HYPOL 2000 to make a

25 homogenuous prepolymer/carbon/additive mixture using a
high torque mechanical mixer. A homogenuous mixture
is indicated when the material has a wet "sheen"
appearance. Two mL of Tween 80 and 10 mL of glacial
acetic acid were added to 5 gals. of bacterial cluture

30 (optical density at 600 nm approx. 0.2). The
bacterial culture then was added to the polyurethane
prepolymer/carbon mixture in the mixing vessel and
mixed rapidly with the high torque mechanical mixer.
At first, the mixture was very viscous but rapidly

35 lost its viscosity and was easily mixed. As the
degree of crosslinking increased, the material once
again began to become viscous. At this stage it is

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very important to stop mechanically mixing the
solution and allow the foaming to proceed. The sodium
bicarbonate and the glacial acetic acid neutralize
each other and in the process generate exogenuous
5 carbon dioxide. This extra gas formation added with
that generated from the HYPOL crosslinking reactions
leads to large and interconnected pores in the
biofoam. The presence of the Tween 80 amplifies this
effect by decreasing interfacial surface tension and
10 promoting foam formation. The foam was usually
alllowed to cure for 10 to 20 minutes before it was
cut up into blocks or shredded in a fitzmill
comminuting machine to produce biofoam blocks of the
desired size. The total volume of biofoam produced
15 from this quantity of prepolymer and bacterial cluture
and produced under the above conditions was between 80
and 100 gallons.

EXAMPLE 7

20   Preparation, Operation, and Performance
Characteristics of Fixed Bed Reactors. Four glass
reactors were used as fixed bed reactors with
different packing material as described in table 1.
Fixed bed reactirs using a bed of biofoam of this
25 invention is referred to as an immobilized cell
bioreactor (ICB). Each bench scale fixed bed reactor
consisted of a glass column of approximately 580 ml
total capacity 64 cm high and 3.4 cm internal
diameter. The reactor volume occupied by water and
30 foam was approximately 480 ml. The biofoam in the
reactors consisted of irregular 3/8" cubic blocks with
the bed held in the reactor by means of 1/14" wire
mesh screens 53 cm apart. Biofoam volume in the
reactor was approximately 350 ml with an internal void
35 volume of 260 ml. The interstitial water volume
between the biofoam blocks was approximately 130 ml.
Reactors were operated in a cocurrent upflow mode,

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i.e., both air and water flowing from the bottom to
the top of the reactor, unless otherwise indicated.
Compressed air (40 psig) was used to aerate the column
throug a sintered glass sparger located at the bottom
5 of the column. A gas regulator was used to regulate
the aeration rate through the sparger at a level
between 4 and 12 L/hr. Wastewater was pumped from a 4
liter feed reservoir to the bottom of the reactor with
a Masterflex peristaltic pump. Typical wastewater
10 flows through the reactor ranged from 0.25 to 0.8
ml/min. The effluent from the columns was collected
in another 4 liter reservoir. Both the feed and
effluent reservoirs were placed in ice baths. The
ambient temperature of the columns was approximately
15 25°C.

TABLE 1

Reactor	Packing/Catalyst	Flowpath
#1	Polypropylene discs, cells allowed to colonize surface (natural biofilm developed).	Upflow
#2	P-1 cells[a] entrapped in polyurethane foam (5g of HYPOL 3000 with 100 mL of P-1 culture	Upflow
#3	P-1 in foam with activated carbon (5g of HYPOL 3000, 25g of ATOCHEM 830 DC[b] and 100 mL of P-1 culture).	Upflow
#4	P-1 in foam with activated carbon as for #3.	Downflow

a.   Yeast cells enriched as described in Example 1 from hydrocarbon
contaminated soil sample from Des Plaines, IL

b.   Powdered activated carbon from Atochem Co.

In each case the feed consisted of an aqueous solution containing 0.1 g/L dibasic potassium phosphate, 0.5 g/L ammonium sulfate, 0.1 g/L magnesium sulfate, 0.05 g/L calcium chloride, 0.01 g/L yeast

5 extract, and 500 mg/L phenol. The phenol present in the effluent from the columns was analyzed by solid phase extraction with cyclohexyl columns supplied by Analytichem Co. by the 4-aminoantipyrine assay (R.D. Yang and A.E. Humphrey, Biotech. and Bioeng., 17,

10 1211-35 (1975)). Suspended solids in the reactor effluents were determined by measuring the optical density at 600 nm. The columns were operated at a liquid hourly space velocity between 0.03 and 0.12 hrs^{-1} for a total period of 116 days at an aeration

15 rate (air introduced at bottom of reactor of 12 liters per hour and an average temperature of 25°C. Results are tabulated in the following tables.

The results in Tables 2-4 will be better a]]recoated of it is understtod that both the

20 particular microbial species present in the reactors and their population are varying through the course of experimentation. With time the microorgansims adapt to the waste stream via natural selection, and the adaptation itself may depend, iter alia, on flow rate

25 (LHSV). The p pulation mix and number means that a steady state may not have been achieved at all flow rates during the courses of experimentation. In fact, since low flow rates were chronologically the earliest experiments it is unlikely that a steady state was

30 achieved at an LHSV of 0.03 hr -1 during the period of sampling. The chief consequence is that comparisons, even within the same reactor, of results at different LHSV are ambiguous.

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– 36 –

TABLE 2

TABLE 2. Effluent Phenol Concentrations in
Immobilized Whole Cell Reactors

LHSV,[a] hr^{-1}	Effluent Phenol Concentration (μg/L)			
	Reactor #1	Reactor #2	Reactor #3	Reactor #4
0.03	73 ± 31	72 ± 40	31 ± 21	31 ± 11
0.06	44 ± 9	45 ± 8	24 ± 12	29 ± 13
0.09	40 ± 16	33 ± 4	18 ± 6	b
0.12	23 ± 8	24 ± 3	12 ± 5	b

a. LHSV = liquid hourly space velocity. Hydraulic retention time (HRT) and
LHSV are reciprocals, i.e., HRT = (1/LHSV)
b. Reactor #4 plugged

TABLE 3

TABLE 3. Effluent Suspended Solids in Immobilized
Whole Cell Reactors

LHSV[a] hr^{-1}	Suspended Solids as O.D. 600 nm			
	Reactor #1	Reactor #2	Reactor #3	Reactor #4
0.03	0.190 ± 0.060	0.030 ± 0.015	0.046 ± 0.020	0.021 ± 0.010
0.06	0.102 ± 0.064	0.062 ± 0.012	0.029 ± 0.020	0.022 ± 0.020
0.09	0.064 ± 0.041	0.052 ± 0.041	0.040 ± 0.012	b
0.12	0.106 ± 0.091	0.048 ± 0.018	0.073 ± 0.034	b

a. LHSV = liquid hourly space velocity. Hydraulic retention time (HRT) and
LHSV are reciprocals, i.e., HRT = (1/LHSV)
b. Reactor #4 plugged

Table 2 shows that at all HRT's the combination of foam having entrapped carbon andmicrooganisms afforded significantly lower phenol effluent levels than the other fixed bed reactors (#1 and #2), especially in
5 achieving phenol effluent levels of 20 ppb and under. The data in Table 3 show that sludge formation, as measured by suspended soluids from our PBSS-packed reactors, was substantially less than that from prior art reactor #1, with reductions ranging from 32 to 76
10 percent. This comparison becomes even more favorable when it is realized that reactor #3 simultaneuously produces lower sludge formation and lower phenol effluent levels than does reactor #1.

15

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TABLE 4

Effluent Phenol Levels from Immobilized
Cell Reactors

DAYS	LHSV, hr^{-1}	EFFLUENT PHENOL CONCENTRATION (μ g/L)			
		Reactor #1	Reactor #2	Reactor #3	Reactor #4
6	0.03	101	110	82	-
7	•	137	171	44	45
11	•	77	73	30	27
12	•	70	58	22	24
13	•	47	47	25	29
14	•	59	68	25	32
22	•	32	41	15	16
25	•	61	44	20	27
29	0.06	43	36	13	19
33	•	47	47	24	22
50	•	58	58	26	23
55	•	48	50	22	22
58	•	40	46	21	23
62	•	30	38	15	18
65	•	47	49	29	28
68	•	32	36	12	**
75	0.09	35	30	13	**
79	•	21	28	12	**
83	•	64	34	17	**
85	•	33	38	24	**
88	•	45	34	23	**
99	0.12	27	26	16	**
103	•	27	24	17	**
106	•	27	25	5	**
116	•	12	19	11	**

** - Reactor #4 plugged

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The foregoing data show that tere is no
significant difference between performance of the
naturally immobilized cell reactor (i.e., where the
cell are attached on the polypropylene surface) and
5   cells immobilized in polypropylene surface) and cells
immmpbilized in polyurethane foam as regards effluent
phenol levels, nevertheless there is lower sludge
formation, as measured by lower suspended solids in
the effluent, from the foam immobilized reactor
10 compared to the biofilm reactor. However, the
presence of activated carbon appears to have a
significant and dramatic effect upon the level of
phenol present in the reactor effluent, permitting
phenol levels at or below 20 ppb.

15

EXAMPLE 8

Pilot Plant Operation. A scaled up version of
reactors 3 and 4 of the foregoing example was used to
process a slip stream of industrail wastewater at a
20 coal tar processing plant. The reactor was 14 feet
high with an inside diameter of 12.4 inches. Foam
prepared as above but contianing approximately 33
weight percent powdered activated carbon was cut into
cubes approximately 1 inch per side ans was used to
25 pack the reactor along with air passed through a
sparging tube. After an extensive shakedown period
during which the effect of various independent
variable supon system orperating performance was
evaluated, the unit was operated at what was
30 determined to be its optimum point forphenol removeal
from the feedstock. This corresponded to a feed flow
rate of 0.1 gallon per minute, or HRT of 15 hours, and
an air flow of 1.15 SFCM.
The pilot plant was operated concurrently with a
35 Leopold Upflow BioTower from Sybron Inc. which
profcessed the industrial waste water from which the
slip stream to the pilort plant was drawn. The

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Bio-Tower was operated under conditions determined to be its optimum for phenol removal, which included an HRT of about 15 hours. The concurrent operation permitted a comparison of operational characteristics

5 between the two units, some of which are summarized in the following tables.

The standard analytical test method for phenols using 4-aminoantipyrine (4-AAP) does not discriminate among individual phenolic components and also has been

10 found to be subject to interference by many non-phenolic materials, such as aromatic hydrocarbons. In contrast, gas chromatographic analysis using a mass selective detector is both more sentsitive and discriminatory than the 4-AAP method,

15 affording more reliable data.

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TABLE 5

GC/MSD Analysis of Phenolics in Wastewater Feed and in Bio-Tower and Pilot Plant Effluents[a]

Sample No.	Component	Concentration (μg/L)		
		Wastewater	ICB Pilot Plant	Sybron Bio-Tower
1	phenol	393,000	14	11
	o-cresol	40,000	31	8
	m,p-cresol	62,000	7	28
	2,4-dimethyl phenol	6,000	9	36
	Phenolics by 4-AAP[b]	800,000	1,100	1,500
2	phenol	541,000	28	25
	o-cresol	42,000	31	201
	m,p-cresol	70,000	10	996
	2,4-dimethyl phenol	5,800	11	241
	Phenolics by 4-AAP	950,000	900	4,400
3	phenol	1,408,333	12	3,907
	2,4 dimethyl phenol	17,545	96	37
	TSS (mg/L)	59	208	1113
4	phenol	339,024	6	801
	2,4-dimethyl phenol	2,665	9	208
	TSS (mg/L)	55	189	760

a.   GC/MSD stands for gas chromatographic analysis with mass selective detector.

b.   4-Aminoantipyrine analysis.

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TABLE 6

Table 6 summarizes analytical results from a commercial environmental laboratory.

TABLE 6. Analytical Results from Independent Laboratory[a]

Pollutants	Feed[b]	Pilot Plant[b] Effluent	Bio-Tower[b] Effluent
2,4-DIMETHYLPHENOL	880	<100	130
PHENOL	240000	<100	<100
ACENAPHTHENE	620	<100	340
ACENAPHTHLENE	122	420	<100
FLUORANTHENE	130	<100	<100
NAPHTHALENE	5000	<100	260
PHENANTHRENE	350	<100	<100
	<400	<100	<100

a.   Kemron Environmental Services, (109 Starlite Park, Marietta, Ohio   45715)

b.   All units are micrograms per liter (μg/L). Detection Limits are: feed = 400; effluent = 100.

The foregoing data show that the method which is our invnetion is at least as efficent as a current commerical process, and is in fact even more efficient in removeal of some non-regulated phenolic materials such as the cresols and, especially, 2,4-dimethylphenol. In particular, it appears to more consistently reduce them to a level under the achieved by the comparison process. In addition, the ICB produced less than 25% of the sludge produced by the

comparison process.

The waste water also contained aromatic
hydrocarbons as pollutants, and Table 7 shows that our
method is as efficient as the ccommercial comparison
5 process in the removal of these materials as well.

TABLE 7

Purge and Trap GC/FID Analysis of Benzene
and Toluene.[a]

Run	Concentration (mass-ppb)					
	Influent Wastewater		Pilot Plant Effluent		Bio-Tower Effluent	
	Benzene	Toluene	Benzene	Toluene	Benzene	Toluene
1	3,800	2,400	25	10	35	10
2	6,200	4,100	35	14	26	8
3	4,800	1,600	12	6	—	—

a.   GC/FID stands for gas chromatograph with flame ionization detector.

EXAMPLE 9

Laboratory Performance with Industrial Waste
Water. A glass reactor as described in Example 7 used
25 as a fixed bed the porous biomass system of Example 1
containing 33 weight percent powdered activated
carbon. The microorganisms entrapped in the biofoam
were enrichement cultures drom the wastewater and soil
at the site prepared as described in Example 6. The
30 reactors (ICB) were operated at a hydraulic retention
time of 24 hours using a sample of industrial waste
water from a phenol production plant. For comparison,
effluent of the same waste water treated with
activated sludege for 120 hours is also shown. Table
35 8 shows that both benzene and pheol are degreaded
almost completely immediately upon operation of the
unit. A second trial afforded similar results. Table

9 shows the effect of hydraulic retention time on
phenol breakthrough, and shows similar phenol
degradation at hydraulic retention times as low as
about 8 hours. As previously noted the penolic assay
5 by 4-aminoantipyrine is subject to interfacence by a
nyriad of substances, including aromatic hydrocarbons,
which are likely to be found in the waste waters.
Therefore the results of they analysis in this table
are to be used solely to indicate a ttrend rather than
10 for absolute purposes. In contrast, Table 10 affords
an analytical result as obtained via GC/MSD analysis
in which the effect of interfering substances has been
removed and which gives much more reliable analysis
then the 4-AAP method. Among other things, Tab;e 10
15 shows the normous reduction in sludge production by
the method of this invention relative to that of a
typical retention basin Finally, Table 11 shows more
complete analytical data for effluent, from which it
can be concluded that our reactor affords more
20 complete degradation of most organic pollutants in 24
hours than does activated sludge in a retentikon basin
in 120 hours.

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TABLE 8

Immobilized Whole Cell Reactor Treatment of an Industrial Waste VT-633. Additional Phenol and Benzene Added.

Time (hours)[d]	23.8	30.3	47.3
Influent Benzene Conc. (ppb)	2644.0	3200.0	920.0
Incremental Total Benzene Loaded (μg)	621.3	294.4	220.8
Incremental Total Effluent Benzene (μg)[b]	< 0.5	< 0.2	< 0.5
Total Trapped Benzene in air (μg)	3.0	0.8	1.7
% Benzene Degraded	> 99.4	> 99.7	> 99.0
Influent Phenolics Conc. (ppm)[a]	141.6	144.8	135.3
Effluent Phenol Conc. (ppm)[b]	bmdl[c]	bmdl[c]	bmdl[c]
% Phenol Degraded	> 99.5	> 99.5	> 99.5

a. Total phenolics by 4-AAP assay.

b. Minimum detection limits: phenol .2 ppm by 4-AAP assay; benzene, 2 parts per billion by purge and trap gas chromatography with flame ionization detector.

c. bmdl = below minimum detection limit.

d. Time from startup.

TABLE 9

Immobilized Whole Cell Reactor Treatment of an Industrial Waste VT-633.

Accumulative Time (hrs):	26.25	52.25	77.25	105.25	123.75	150.08	173.08	198.08	224.08
Elapsed Time (hrs):	26.25	26.00	25.00	28.00	18.50	26.33	25.00	25.00	26.00
HRT (hr/col):	23.3	25.4	23.3	11.0	11.0	10.6	8.7	8.6	7.2
Influent Total Phenolics Conc.(ppm):	66.7	43.0	45.9	45.7	45.2	45.5	45.7	50.6	54.7
Effluent Phenol Conc.(ppm):	2.0	3.5	3.7	3.6	4.0	3.8	3.6	3.7	6.3
% Phenol Degraded:	97.0	91.9	91.9	92.1	91.2	91.6	92.1	92.7	88.5

TABLE 10

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Analysis of Untreated, ICB Treated and
Activated Sludge Treated Wastewater

Component	Concentration (ppb)		
	Untreated	ICB	Activated Sludge
Acetone	1,350,000	100,000	850,000
Phenol	35,000	10	10
Benzene	350	20	20

ICB	-	24 hr retention time
	-	0.58 mg. sludge/liter effluent
Activated Sludge	-	120 hr. retention time
	-	1.75 mg sludge/liter effluent

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TABLE 11. Water Analyses Results, ppb

Compound	ICB Reactor	Active Sludge
Acetone	100,000	850,000
Benzene	20	20
Butanone	<10	200
Pentanone	<10	300
Chloroform	300	200
Epoxy ketone	600	. 3000
Diacetone alcohol	350	1700
C_9 ketone?	2000	4000
Methyl cyclohexenone	700	3500
Dimethyl phenyl carbinol	60,000	200,000
Acetophenone	<10	10,000
Acetyl cyclohexanone	300	3500
Unknown M. W. 126	100	75
Phenol	10	10

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EXAMPLE 10

Comparison of Reactor Configuratikon on Sludge
Production. A model wastewater feed (described in
5 Example 7) was treated in three bench scale reactors.
Two were 500 ml New Brunswich glass fermenters that
were continuously mixed with a mechanical stirrer.
One of these fermentors were continuously mixed with a
mechanical stirrer. One of these fermentros were
10 operated as a chemostat in which the wastewater was
pumped through with ahydraulic retentikon time of 33
hours. In this reactor in the effluent. A second
mixed reactor was filled with approximately 200 ml of
biofoam and operated similarly. The third reactor
15 consisted of a 500 mil ICB bench scale reactor, as
described in Example 1, using as a fixed bed the same
biofoam as used in the foregoing second mixed
reactor. This reactor was operated with a hydraulic
retention time of 12.5 hours. The ICB reactor
20 produced both lower sludge and better phenol removal
efficiency then either of the mixed reactors, as shown
in Table 12.

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Table 12. Sludge Formation in Various Reactors

Reactor	HRT (hrs)	Effluent Phenol[c] (μg/L)	Sludge[c]	
			OD 600 nm[a]	TSS (mg/L)[b]
Continuous Stirred Tank Reactor (CSTR)	33	820	0.45	680
CSTR + Biofoam	33	62	0.36	606
ICB	13	19	0.07	96

a.   Sludge as measured by turbidity; optional density at 600 nm.
b.   Total suspended solids.
c.   Measurements taken after 1 void volume for the CSTR reactors, and after 33 hours for the ICB. None represent steady state conditions.

These data clearly and unambiguously show a substantial, quite significant reduction in sludge production using our biofoam in a fixed bed reactor.

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WHAT IS CLAIMED IS

1.   A biomass support system comprising a hydrophilic polyurethane foam and activated carbon.

2.   The support system of claim 1 wherein hydrophilic
5 polyurethane foam is prepared from a polyisocyanate compound and a polyol wherein at least 80% by weight of the polyol content is polyethylene oxide.

3.   The support system of claim 2 wherein the polyol is at least 90% by weight polyethylene oxide.

10   4.   The support system of claim 3 wherein the polyol content is greater than about 99% by weight polyethylene axide.

5.   The support system of claim 2 wherein the polyisocyanate component contains from about 1 to less
15 than about 25% by weight aromatic isocyanate.

6.   The support system of claim 3 wherein the aromatic isocyanate content ranges from about 1 to less 20% by weight.

7.   The support system of claim 4 wherein the aromatic
20 isocyanate content ranges from about 1 to less than about 15% by weight.

8.   The support system of claim 1 wherein said activated carbon is selected from wood charcoal and anthracite coal.

25   9.   The support system of claim 8 wherein the activated carbon is wood charcoal.

10.   The support system of claim 1 wherein said activated charcoal has a K_d value ranging from about 0.001 mg/L to about 300 mg/L.

30   11.   A porous biomass support comprising (i) a hydrophilic polyurethane foam, (ii) activated carbon and (iii) a phenolic degrading microorganisms; said activated carbon and microorganisms having K_d and K_s values in order that the K_s/K_d ratio is between about 1:1 and about 1:50.

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12.   A method for the aerobic biodegration of phenolic
materials in aqueous streams to a level under 0.1 parts
per million in a period of no more than 30 hours
comprising flowing an aqueous materials in the presence of
5 oxygen through a fixed mass of the porous biomass support
system of claim 1.

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Figure 1. Adsorption Curves for Foams and Carbon Impregnated Foams

g Phenol adsorbed/ g Foam

Equilibrium Phenol Concentration (mg/L)

—+— Hydrophilic Foam

—*— Hydrophobic Foam

—+— Hydrophilic + PAC

—□— Hydrophobic + PAC

20% PAC In Foam

0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
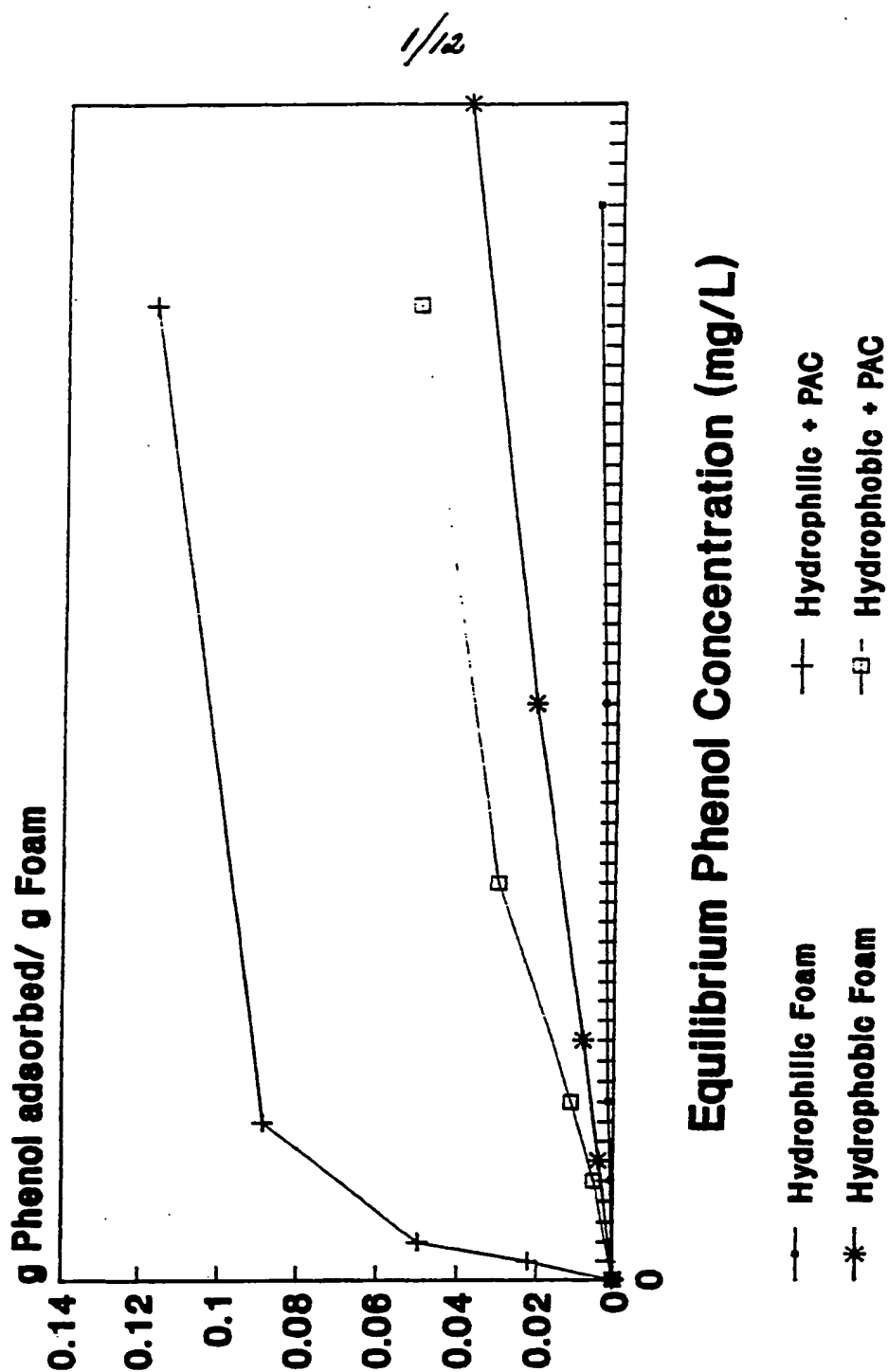
Figure 2. Adsorption Curves for Hydrophilic Foam & Carbon Impregnated Foam

Equilibrium Phenol Concentration (mg/L)

g Phenol adsorbed/ g Foam

—— Hydrophilic Foam   —+— Hydrophilic + PAC

20% PAC In Foam

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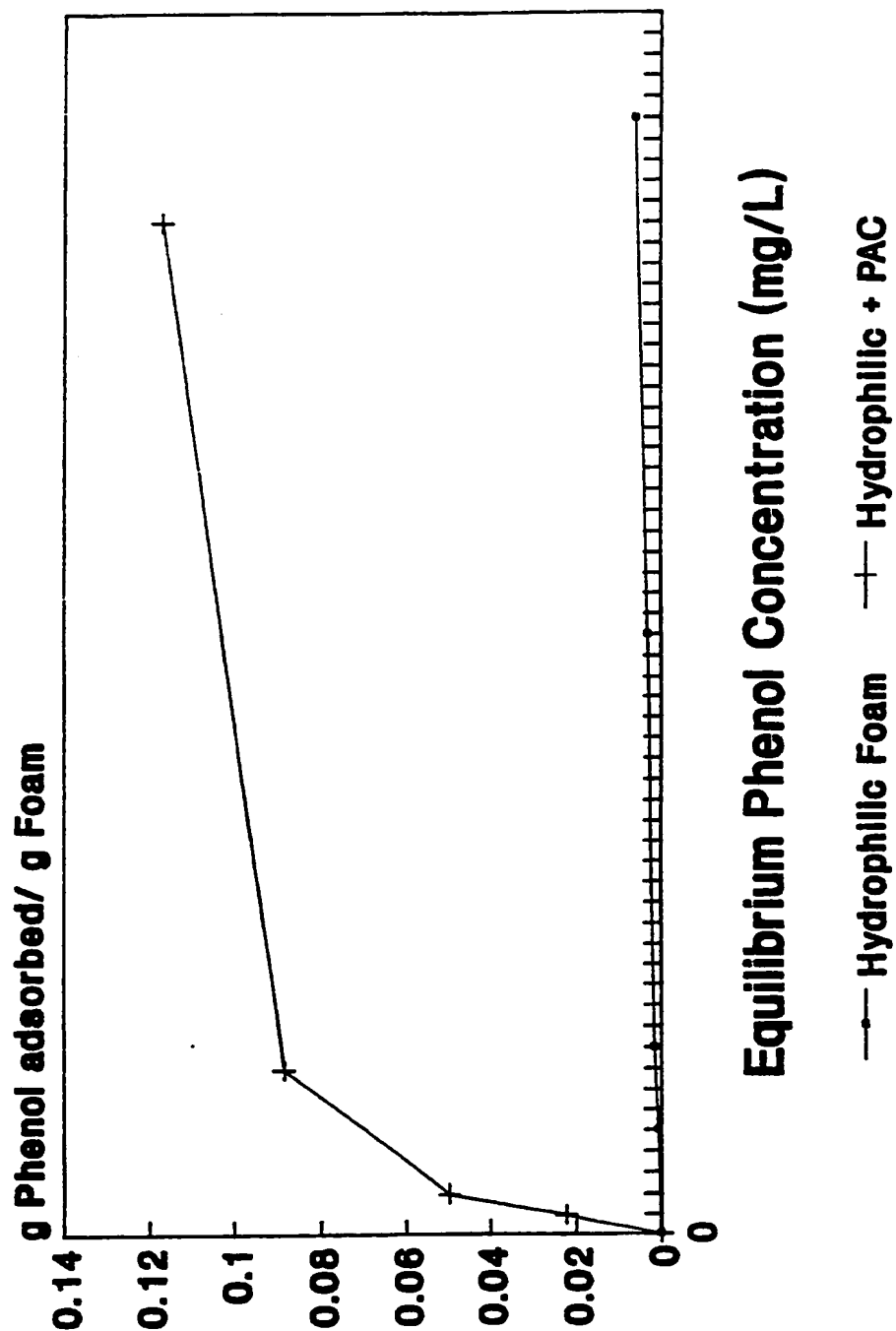
Figure 3. Adsorption Curves for Hydrophobic Foam and Carbon Impregnated Foam

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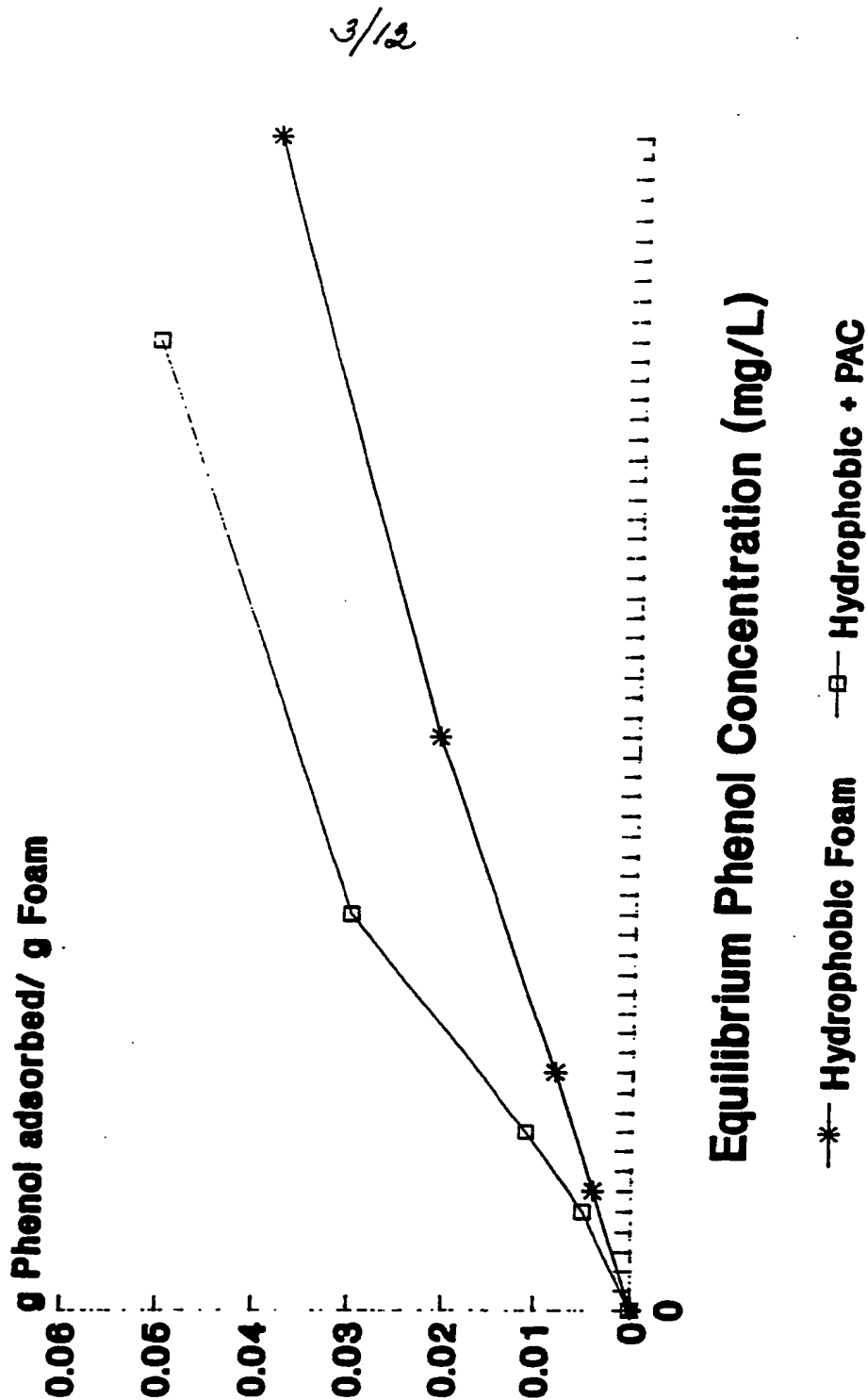
Figure 4

FIGURE 4a. 1-PULSE C-13-NMR OF ICB SYSTEM (All phenol — includes both mobile and solid or tightly bound phenol).

FIGURE 4b. CPMAS C-13 NMR OF ICB SYSTEM (Solid or tightly bound phenol only).

Mobile Segments Polyol Chains $+O\sim O\sim O\sim)_n$

Phenol on Carbon Support

Phenol in Foam

Aqueous Phenol

a.

Rigid Segments Polyol Chains $+O\sim O\sim O\sim)_n$ on Hypol foam.

Phenol on Carbon Support

b.

158.14

79.07

PPM
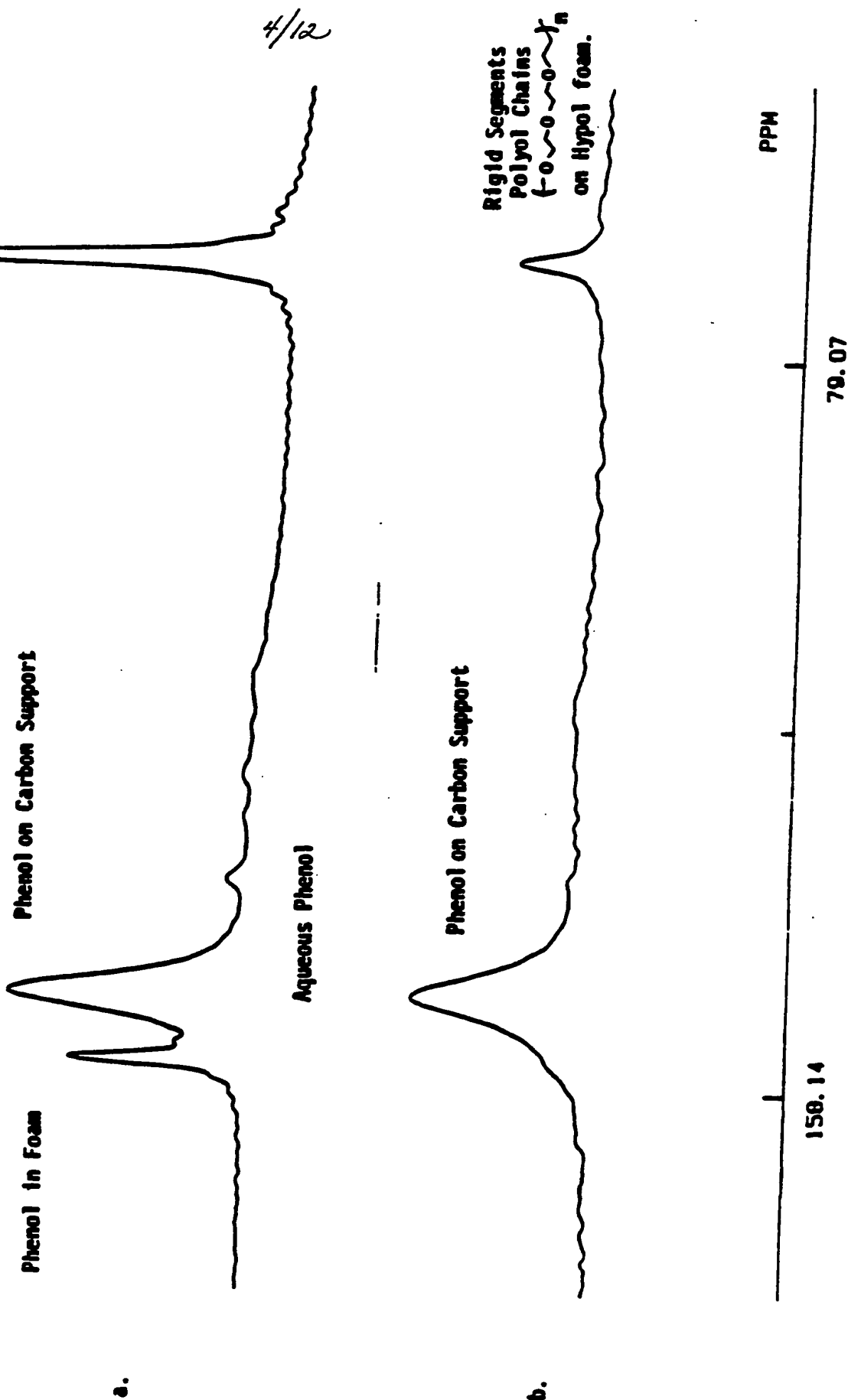
Figure 5

FIGURE 5a.　CPMAS C-13 NMR OF
HYPOL FOAM.

FIGURE 5b.　CPMAS C-13 NMR OF
GENERAL FOAM.

CPMAS OF HYPOL FOAM

Rigid segments of polyols of Hypol
foam.

Rigid aromatic segments are
in low concentration in
Hypol foam.
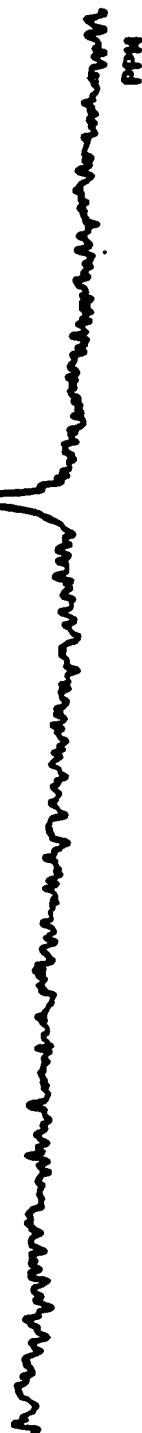
CPMAS OF GENERAL FOAM

Rigid segments of alkyl chains
in General foam.

Rigid segments of rigid segments in
General foam.

Rigid aromatic segments are in
higher concentration in General foam.

PPM

160.97　　120.73　　80.49　　40.24　　-0.00

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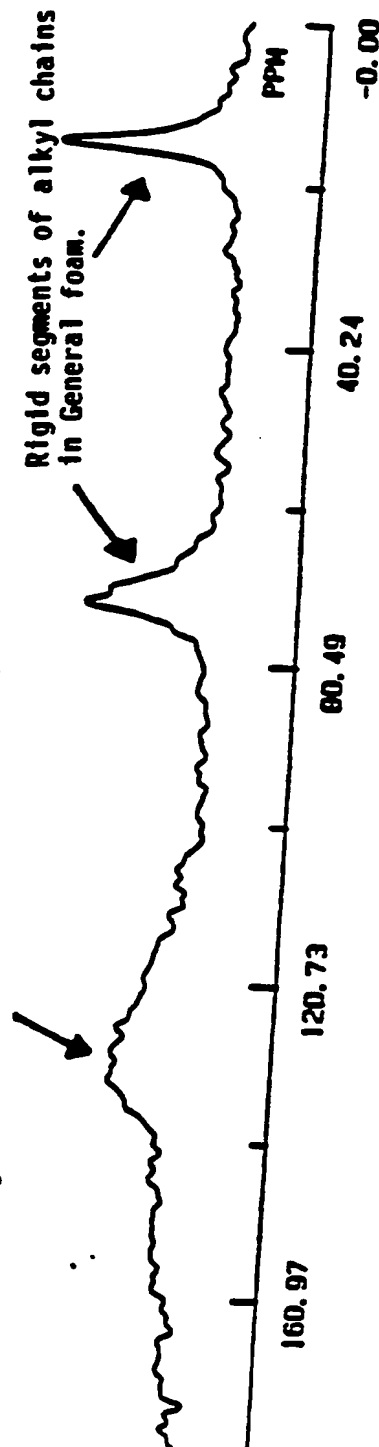
FIGURE 6

PHENOL ADSORPTION ON
CARBON \HYPOL AND CARBON
\GENERAL FOAM
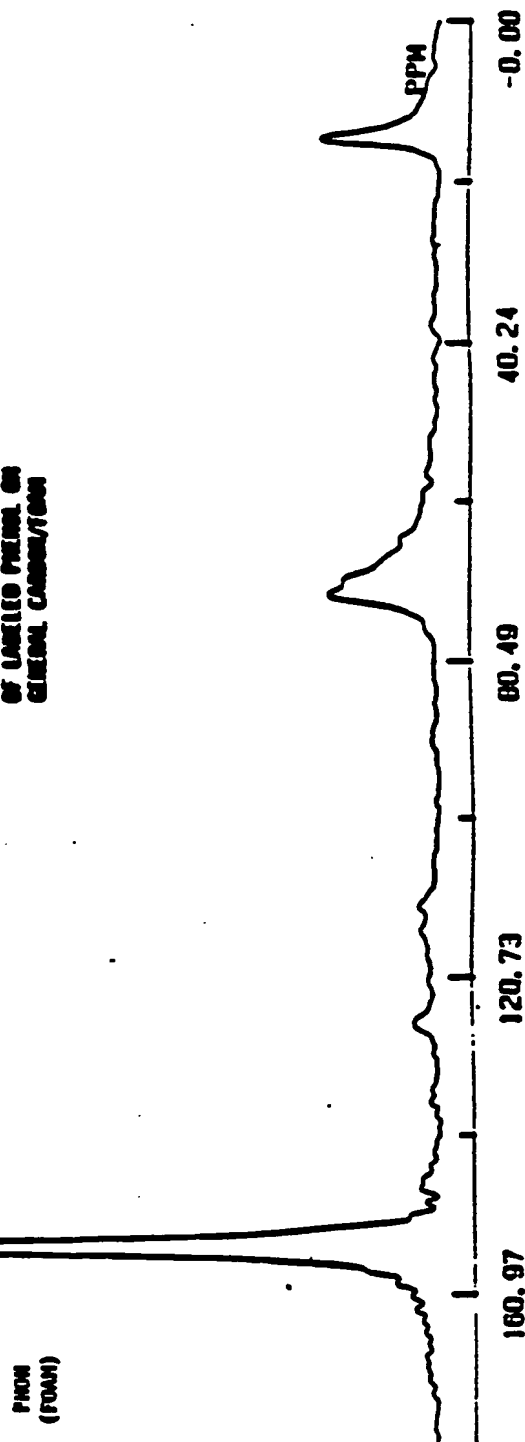
7/12

Figure 7
Summary From C-13 NMR Results

8/12
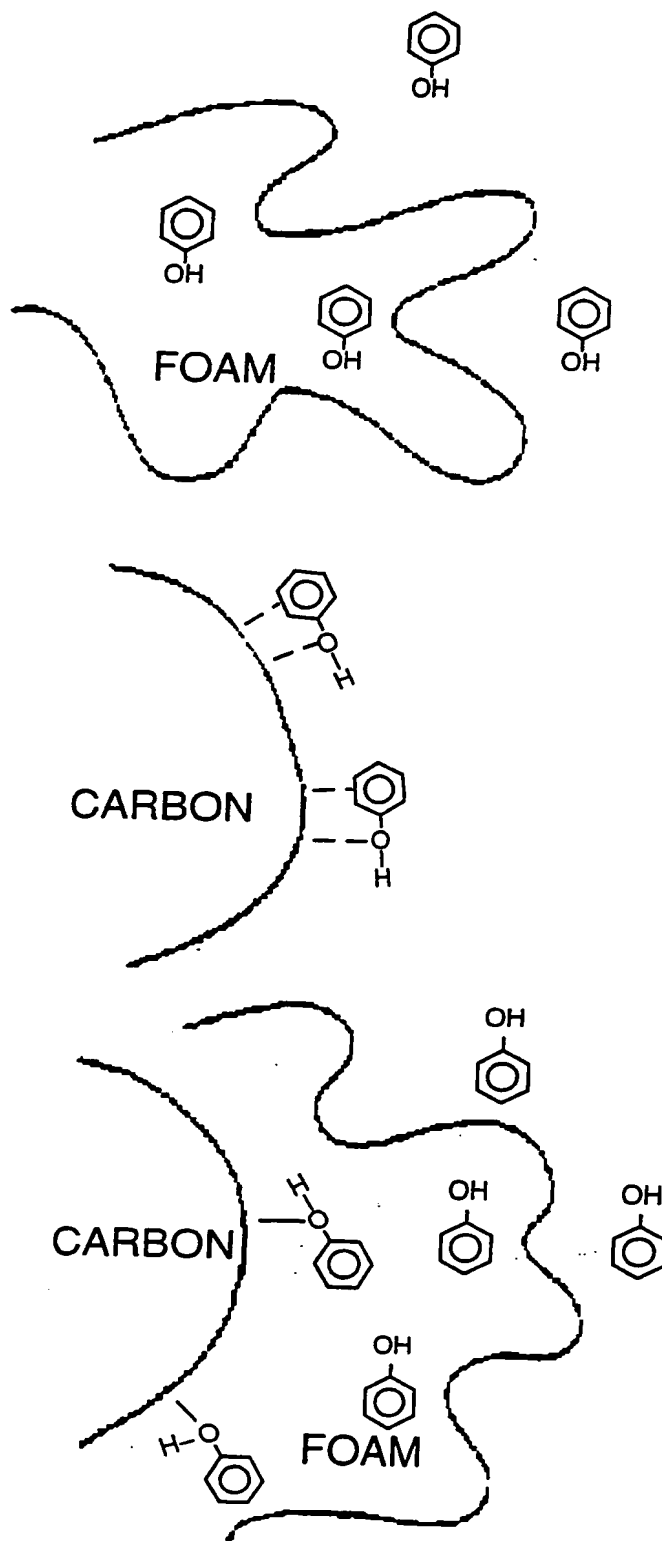
Figure 8. Response of Bioreactors Containing PUF Supports to Shock Loads of Phenol

9/12
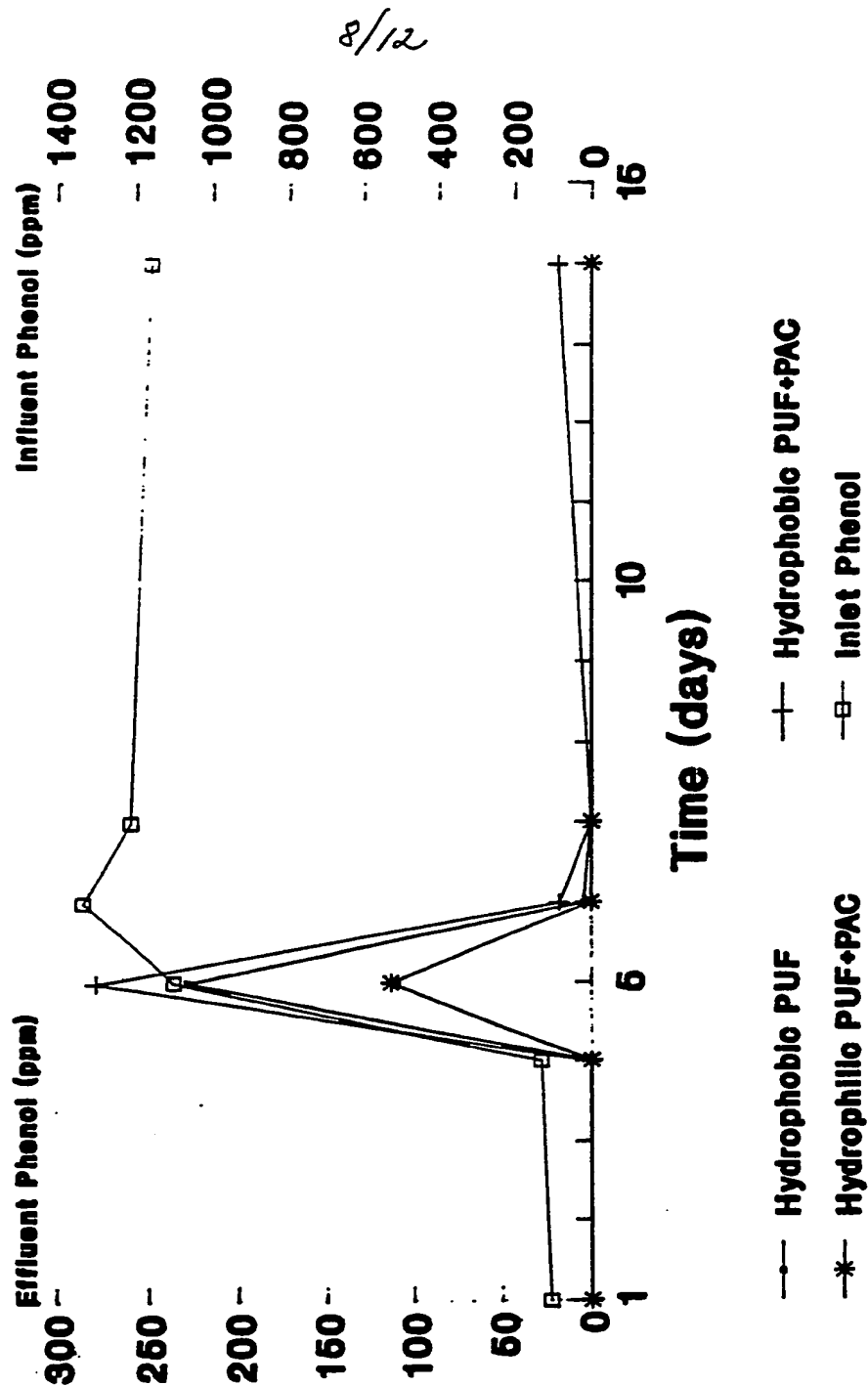
Figure 9. Total Phenolics Removal by Bioreactors using Polyurethane Foam Supports

10/12

Figure 10. Aromatic Pollutant Removal by
Reactors Using Polyurethane
Foam Supports
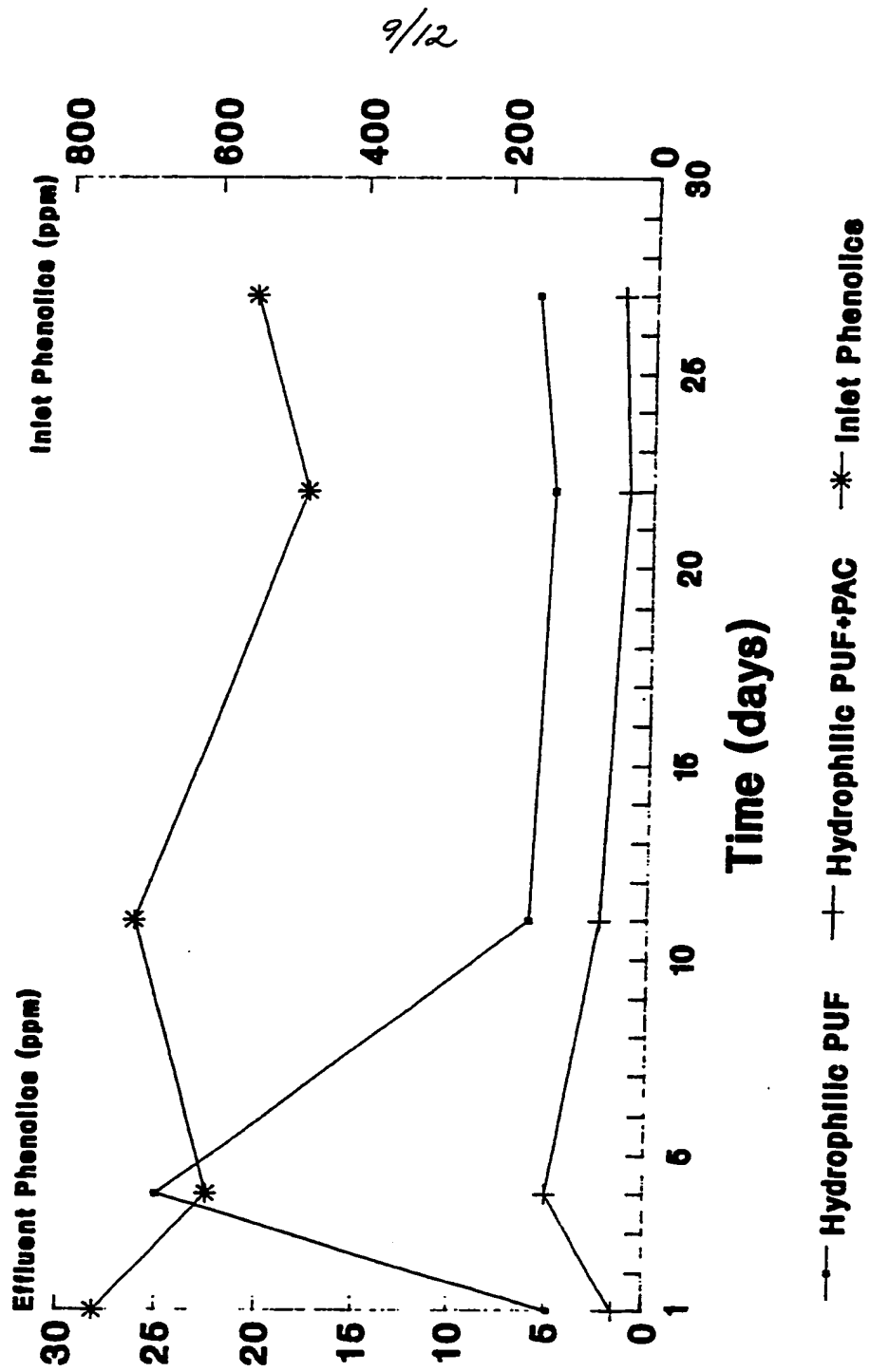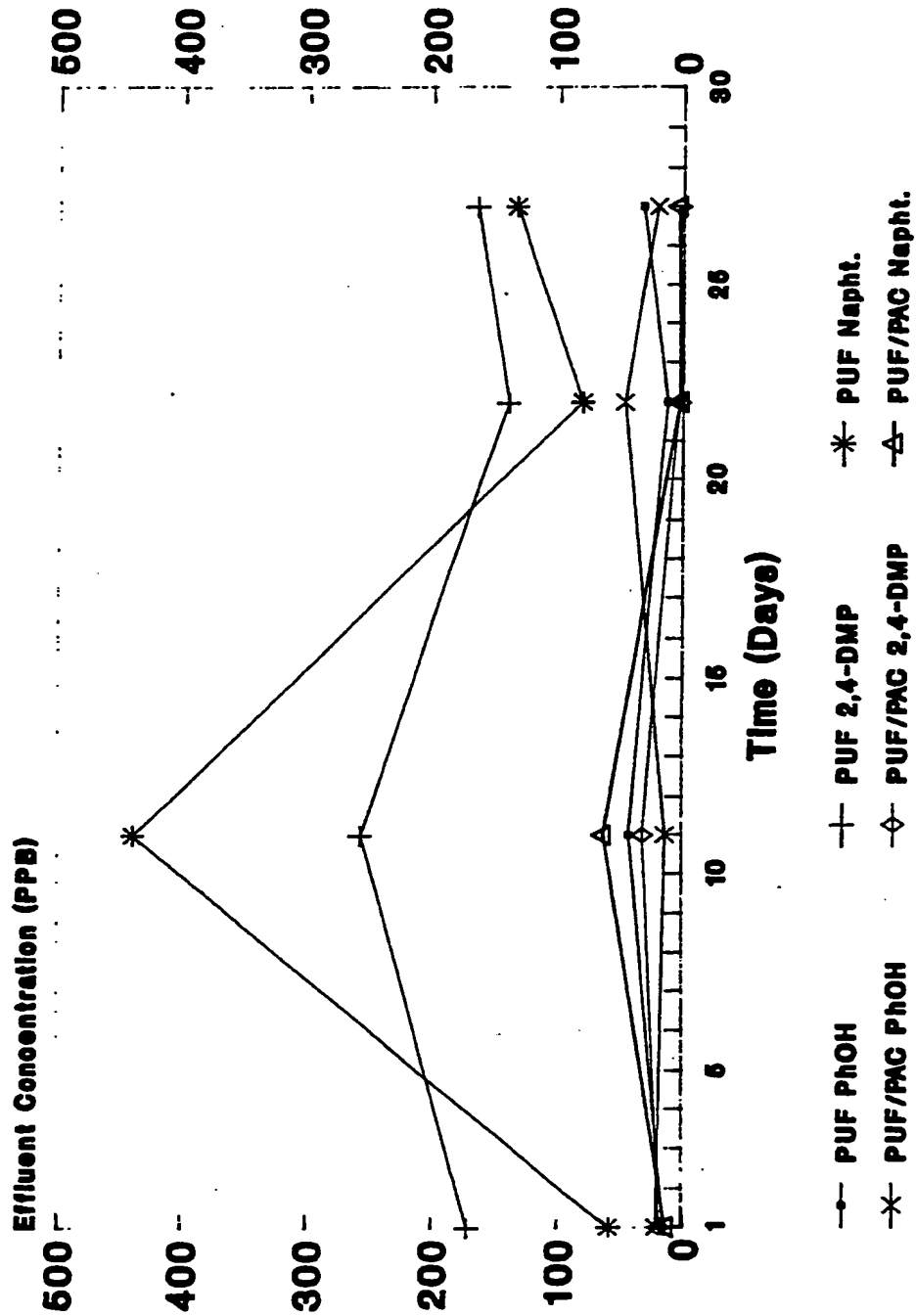
Coal Tar Processing Plant Wastewater

Figure 11
SEM Photographs Of Carbon Impregnated In Bulk Foam
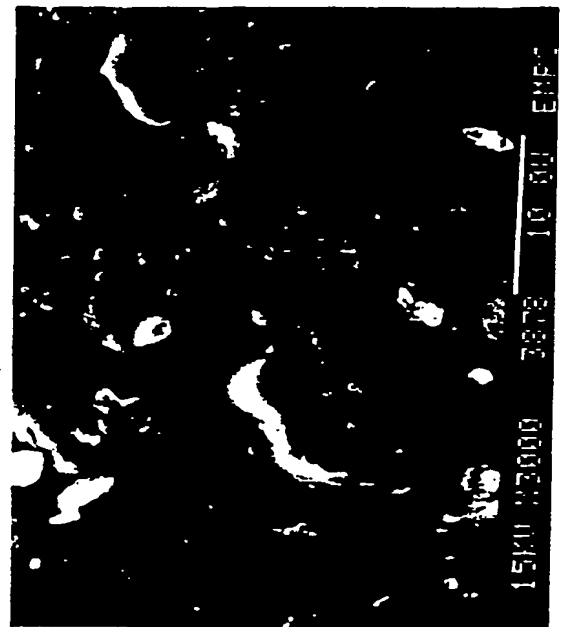
12/12

Figure 12
SEM Photographs Of Carbon Surface-Impregnated
Using Ethyl Acetate Solvent

INTERNATIONAL SEARCH REPORT

PCT/US 91/07436

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C02F3/10;   C08G18/48

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	CO2F ; C08G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 150 747 (BAYER) 7 August 1985 see page 79; claim 1 see page 23, line 12 - line 26 see page 24, line 23 - page 25, line 7 see page 33, line 11 - line 25 see page 43 - page 46, line 3 see page 64; example 7	1,5,6,8
A		2-4,11, 12

P,X	WO,A,9 011 970 (ALLIED-SIGNAL INC.) 18 October 1990 cited in the application see page 56; claims 1,6 see page 20, line 13 - page 21, line 17 see page 25, line 28 - page 26, line 31 see page 28, line 35 - page 29, line 21	1,8,12
A		2-7,11

	-/--	

* Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03 MARCH 1992	1 1. 03. 92

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	TEPLY J.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 781 231 (MINNESOTA MINING AND MANUFACTURING COMPANY) 25 December 1973 see column 8; claims 1,2 see column 6, line 10 - line 20	1-4

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		CA-A-	1249674	31-01-89
		JP-A-	60172399	05-09-85
		US-A-	4576718	18-03-86
WO-A-9011970	18-10-90	US-A-	4983299	08-01-91
		CA-A-	2014030	10-10-90
		EP-A-	0467969	29-01-92
US-A-3781231	25-12-73	None		

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82